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Titanium complexes with chiral amino alcohol ligands: synthesis and structure of complexes related to hydroamination catalysts

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Abstract

Titanium complexes with chiral amino alcohol ligands are useful precatalysts for the intramolecular hydroamination of aminoallenes. They can be synthesized via protonolysis of titanium dimethylamide starting materials with the free ligand. In most cases, the resulting materials are not isolable due to their oily nature. However, several complexes were prepared in pure form and isolated as solid materials. $[Ti(Cl)(NMe_2)(–OCH_2CH(Ph)N(CHMe_2)–]_2$ was prepared at room temperature from $TiCl(NMe_2)_3$ and the corresponding *N*-substituted D-amino alcohol; the dimeric nature of the complex was established by X-ray crystallography. $[Ti(NMe_2)_2(–OCH_2CH(Ph)N(2\text{-Ad})–)]_2$ (2-Ad = 2-Adamantyl) was prepared from $Ti(NMe_2)_4$ and the corresponding *N*-substituted L-amino alcohol after prolonged heating. An intermediate complex that could not be purified or isolated is believed to be $Ti(NMe_2)_3(–OCH_2CH(Ph)NH(2\text{-Ad}))$. Two complexes with the composition $TiCl_2(–OCH_2CH(R^*)N(CHMe_2)–)(HNMe_2)$ (where $R^* = CH_2Ph$ or $CHMe_2$) were prepared at room temperature by protonolysis of $TiCl_2(NMe_2)_2$ with the corresponding *N*-substituted L-amino alcohols. These two complexes exhibit dynamic behavior on the NMR timescale that is believed to be a dimer–monomer equilibrium, but they decompose at elevated temperatures.

Keywords: Titanium; Crystal structures; Amino alcohol complexes

1. Introduction

The organometallic chemistry of the early transition metals is dominated by complexes containing the cyclopentadienyl group (Cp) and its derivatives [1]. There is substantial interest in alternative ligands, such as amides [2–4], alkoxides [5], aryloxides [6–8], sulfonamides [9–12], and amidinates [13], since the dramatically different steric and electronic environments they provide can result in novel reactivity of the resulting complexes [14]. Amide and mixed amide–alkoxide ligands show increased coordinative unsaturation relative to Cp complexes since both ligand types occupy only a single coordination site at the metal per donor atom. These ligands also provide highly tunable electronic and steric environments to a reactive metal center.

The hydroamination reaction (direct addition of an N–H bond across a C–C multiple bond) is one reaction that is currently under wide investigation, as it is a highly atom economical method of synthesizing substituted amines. The development and study of new ligands has led to enhanced or altered catalyst performance. The inter- and intramolecular hydroamination of alkenes and alkynes has been the subject of

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several comprehensive reviews [15–21], including a review of enantioselective catalytic hydroamination of alkenes [22]. The intramolecular hydroamination of aminoallenes has been the focus of less attention. Silver, mercury and palladium catalysts were described more than 20 years ago [23–26], organolanthanide complexes have been studied at length by Marks and coworkers [27–29], and Bergman recently investigated Cp, amide and sulfonamide derived catalysts for the intramolecular hydroamination of alkynes and allenes [30,31].

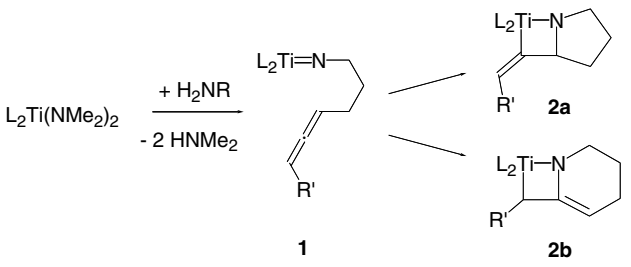
We recently reported the catalytic intramolecular hydroamination of aminoallenes by in situ prepared titanium complexes of a family of readily prepared N-, O-donor ligands [32]. These ligands are prepared in a few steps from the chiral amino acids valine (Val), phenylalanine (Phe) and phenylglycine (Phg) [32,33]. The precatalysts, believed to have the structure $[TiL_2(NMe_2)_2]_2$, can react with a terminal amine to form an imido complex **1** (Scheme 1). The proposed mechanistic step crucial for determining the product distribution is a [2 + 2] cycloaddition reaction of the transient titanium imido complex **1** to form the corresponding azametallacyclobutane **2**. The mechanism of this and the related intermolecular reaction catalyzed by titanium has been studied in detail by Bergman [30,31,34–38].

We sought to understand the nature of our in situ catalysts by initiating a synthetic study. The study was hampered by the poor crystallinity properties of the Ti complexes with most of the ligands. After much effort, several complexes were prepared and isolated, allowing a deeper understanding of the coordination chemistry of titanium with these ligands.

2. Experimental

2.1. General details

All reagents were obtained from commercial suppliers and were purified by standard methods [39], or used as received. Solvents were degassed and distilled from sodium/benzophenone and stored under nitrogen. All air and/or moisture sensitive compounds were manipulated under an atmosphere of nitrogen using standard Schlenk techniques, or in a glove box (MBraun UNIlab). The ligands D-H_2PhgPrO, L-H_2PhgAdO, L-H_2ValPrO and L-H_2PhePrO were prepared by the established procedures [32,33]. Microanalyses were performed by Desert Analytics (Tucson, AZ). All NMR spectra were recorded at ambient temperature on a Brüker Avance 400 spectrometer unless otherwise noted. Carbon assignments were made using DEPT experiments. Melting points were taken on a Meltemp melting apparatus and are uncorrected.



Scheme 1.

2.2. Preparations

2.2.1. TiCl(D-PhgPrO)(NMe_2) (3)

In the glove box, D-H_2PhgPrO (0.502 g, 2.80 mmol), was dissolved in ether (10 mL). This solution was added to a solution of $TiCl(NMe_2)_3$ (0.606 g, 2.81 mmol) in ether (5 mL) and the reaction mixture was allowed to stir overnight, resulting in the formation of an orange precipitate. The reaction mixture was concentrated and the precipitate was collected via vacuum filtration (0.260 g, 0.85 mmol, 30% yield). The crude product was recrystallized from hexane and the resulting precipitate was collected by vacuum filtration giving **3** as a bright orange powder. M.p. 191–192 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.37 (m, 3H, ArH), 7.25 (m, 2H, ArH), 5.299 (sept., J = 6.8 Hz, 1H, $CHMe_2$); 5.25 (m, 2H), 4.522 (d, J = 4.8 Hz, 1H), 3.221 (s, 6H, $N(CH_3)_2$), 1.222 (d, J = 6.8, 3H, CH_3), 0.948 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ = 146.0 (4° Ar), 129.0 (CH), 127.6 (CH), 127.2 (CH), 87.4 (CH_2), 71.8 (CH), 54.9 (CH), 48.1 (CH_3), 22.8 (CH_3), 22.3 (CH_3). *Anal.* Calc. for $C_{13}H_{21}ClN_2OTi$: C, 51.25; H, 6.95; N, 9.20. Found: C, 51.00; H, 6.70; N, 8.94%.

2.2.2. Ti(L-PhgAdO)(NMe_2)$_2$ (4)

In the glove box, L-H_2PhgAdO (1.256 g, 4.63 mmol) was dissolved in toluene (20 mL) and added slowly to a solution of $Ti(NMe_2)_4$ (1.053 g, 4.70 mmol) in toluene (20 mL) in a Teflon valved glass reaction vessel. The vessel was removed from glove box and heated in an oil bath at 110 °C overnight. Most of the solvent was removed in vacuo and complex **4** was isolated as a fine yellow precipitate via vacuum filtration (0.195 g, 0.48 mmol, 10% yield). The material was recrystallized from $(Me_3Si)_2O$ to yield small yellow microcrystals. M.p. 231–232 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.520 (m, 2H, Ar*H*), 7.358 (d, J = 7.2, 2H, Ar*H*), 7.296 (m, 1H, Ar*H*), 5.005 (dd, J = 5.2, 9.2 Hz, 1H, C*H*), 4.777 (d, J = 4.8 Hz, 1H, C*H*), 4.183 (d, J = 9.2 Hz, 1H, C*H*), 3.627 (br s, 1H, C*H*), 3.325 (s, 6H, $N(CH_3)_2$), 2.890 (s, 6H, $N(CH_3)_2$), 2.764 (br d, J = 12.4 Hz, 1H, C*H*), 2.3–1.3 (m, 13H, Ad). ^{13}C NMR (100 MHz, C_6D_6): δ = 147.2 (4° Ar), 128.5 (CH), 127.6 (CH), 126.8 (CH),

78.6 (CH_2), 71.7 (CH), 68.6 (CH), 47.4 (CH_3), 44.6 (CH_3), 39.5 (CH_2), 38.8 (CH_2), 35.5 (CH), 33.0 (CH), 32.6 (CH_2), 31.7 (CH), 28.7 (CH), 28.4 (CH). *Anal*. Calc. for $C_{22}H_{35}N_3OTi$: C, 65.18; H, 8.70; N, 10.37. Found: C, 64.78; H, 8.55; N, 9.98%.

2.2.3. $TiCl_2$(L-PhePrO)($HNMe_2$) (**5a**)

In the glove box, L-H_2PhePrO (0.225 g, 1.14 mmol) was dissolved in ether (5 mL) and added to a stirring solution of $Cl_2Ti(NMe_2)_2$ (0.237 g, 1.15 mmol) in ether (10 mL). A light brown precipitate formed immediately. The solution was allowed to stir overnight at room temperature and complex **5a** was collected via vacuum filtration (0.373 g, 1.05 mmol, 92%). M.p. 134–135 °C. NMR assignments at low temperature are based on both 1-D and 2-D (COSY) spectra. ^{1}H NMR (400 MHz, CD_2Cl_2, −5 °C): δ = 7.322 (m, 4H, ArH), 7.1234 (m, 2H, ArH), 7.173 (d, J = 6.8 Hz, 2H, ArH), 7.034 (d, J = 7.2 Hz, 2H, ArH), 6.402 (septet, J = 6.8 Hz, 1H, C*H*), 6.063 (septet, J = 6.8 Hz, 1H, C*H*), 4.950 (m, 2H, CH_2 and NH), 4.704 (dd, J = 5.4, 11 Hz, 1H, C*H*), 4.546 (m, 2H, CH_2 and NH), 4.318 (d, J = 11.2, 1H, C*H*), 4.206 (dd, J = 6, 11 Hz, 1H, C*H*), 3.980 (m, 1H, C*H*), 2.8 (m, 3H), 2.899 (d, J = 6 Hz, 3H, HN(CH_3)$_2$), 2.682 (d, J = 6 Hz, 3H, HN(CH_3)$_2$), 2.632 (d, J = 5.6 Hz, 3H, HN(CH_3)$_2$), 2.465 (t, J = 12.4 Hz, 1H, CH_2), 2.268 (d, J = 5.6 Hz, 3H, HN(CH_3)$_2$), 1.794 (d, J = 6.8 Hz, 3H, CH_3), 1.568 (d, J = 6.8 Hz, 3H, CH_3), 1.386 (d, J = 6.4 Hz, 3H, CH_3), 1.281 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, C_6D_6, −5 °C): δ = 138.4 (4°), 137.1 (4°), 129.3 (CH), 129.2 (CH), 128.7 (CH), 127.5 (CH), 127.1 (CH), 81.8 (CH_2), 78.8 (CH_2), 71.0 (CH), 70.9 (CH), 63.1 (CH), 58.5 (CH), 47.0 (HN(CH_3)$_2$), 44.6 (HN(CH_3)$_2$), 42.4 (HN(CH_3)$_2$), 42.2 (HN(CH_3)$_2$), 41.0 (CH_2), 39.4 (CH_2), 25.9 (CH_3), 22.8 (CH_3), 21.9 (CH_3), 17.1 (CH_3). *Anal*. Calc. for $C_{14}H_{24}Cl_2N_2OTi$: C, 47.35; H, 6.81; N, 7.89. Found: C, 47.37; H, 6.70; N, 8.20%.

2.2.4. $TiCl_2$(L-ValPrO)($HNMe_2$) (**5b**)

In the glove box, L-H_2ValPrO (0.182 g, 1.25 mmol) was dissolved in ether (5 mL) and added to a stirring solution of $Cl_2Ti(NMe_2)_2$ (0.273 g, 1.32 mmol) in ether (12 mL). A dark brown precipitate formed immediately. The solution was allowed to stir overnight at room temperature and complex **5b** was collected via vacuum filtration (0.142 g, 0.40 mmol, 32%). M.p. 100–102 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, −25 °C): δ = 6.3–6.4 (br m, 2H, $CHMe_2$); 5.2 (m, 2H); 4.7 (br septet, 1H, $CHMe_2$); 4.5 (m, 2H); 4.4 (br septet, 1H, $CHMe_2$); 4.3 (br s, 1H, NH); 4.0 (br s, 1H, NH) 2.789 (d, J = 6.4 Hz, 3H, NMe); 2.612 (d, J = 6 Hz, 3H, NMe); 2.420 (d, J = 5.6 Hz, 3H, NMe); 2.396 (d, J = 5.6 Hz, 3H, NMe); 1.664 (d, J = 6.8 Hz, 3H, $CHMe_2$); 1.421 (d, J = 6.8 Hz, 3H, $CHMe_2$); 1.254 (d, J = 6.8 Hz, 3H, $CHMe_2$); 1.132 (d, J = 7.2 Hz, 3H, $CHMe_2$); 1.009 (d, J = 6.8 Hz, 3H, $CHMe_2$); 0.954 (d, J = 6.8 Hz, 3H, $CHMe_2$); 0.847 (d, J = 6.8 Hz, 3H, $CHMe_2$); 0.758 (d, J = 6.8 Hz, 3H, $CHMe_2$). ^{13}C NMR (100 MHz, CD_2Cl_2, −25 °C): δ = 77.73 (CH_2), 77.37 (CH_2), 75.99 (CH), 75.34 (CH), 61.03 (CH), 58.18 (CH), 46.24 (HN(CH_3)$_2$), 43.71 (HN(CH_3)$_2$), 42.65 (HN(CH_3)$_2$), 42.57 (HN(CH_3)$_2$), 35.70 (CH), 33.35 (CH), 30.66 (CH_3), 24.19 (CH_3), 22.74 (CH_3), 21.15 (CH_3), 20.39 (CH_3), 19.88 (CH_3), 16.89 (CH_3), 16.72 (CH_3). *Anal.* Calc. for $C_{10}H_{23}Cl_2N_2OTi$: C, 39.24; H, 7.57; N, 9.15. Found: C, 38.95, H, 7.77, N, 9.51%.

2.3. X-ray crystal structure determination for $TiCl$(D-PhgPrO)(NMe_2) (**3**)

Suitable crystals were obtained by prolonged storage of a saturated ether solution at −35 °C. An amber block with approximate dimensions of 0.20 × 0.25 × 0.25 mm, was used for the X-ray crystallographic analysis. Diffraction intensity data were collected at 213(2) K using a Brüker Smart Apex CCD diffractometer equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube. Crystal data and refinement parameters are summarized in Table 2. The systematic absences in the diffraction data are consistent with the monoclinic space group options $P2_1$ and $P2_1/m$. *E* statistics suggested the non-centrosymmetric space group, which yielded a chemically reasonable and computationally stable result. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. The correct absolute structure was unambiguously determined, Flack parameter = 0.002(12). Data were corrected for absorption effects using SADABS [40]. The ratio of minimum to maximum apparent transmission was 0.753. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (6.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

3. Results and discussion

Titanium complexes with the amino alcohol ligands shown in Fig. 1 (among others) were prepared in situ for the intramolecular hydroamination of 1,3-disubstituted- and 1,1,3-trisubstituted aminoallenes [32]. The precatalyst was postulated to be the dimeric [Ti(NMe_2)$_2$(L_2)]$_2$ based on the similar NMR resonances to the related [TiCl(NMe_2)(L_2)]$_2$ complexes previously reported [33]. A synthetic study was undertaken in order to more fully understand the coordination chemistry of titanium with these ligands.

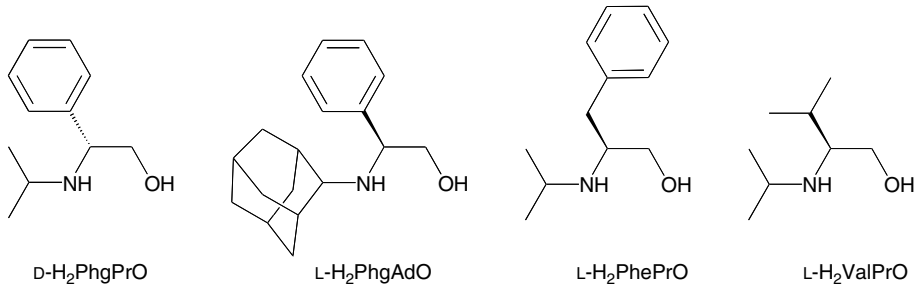


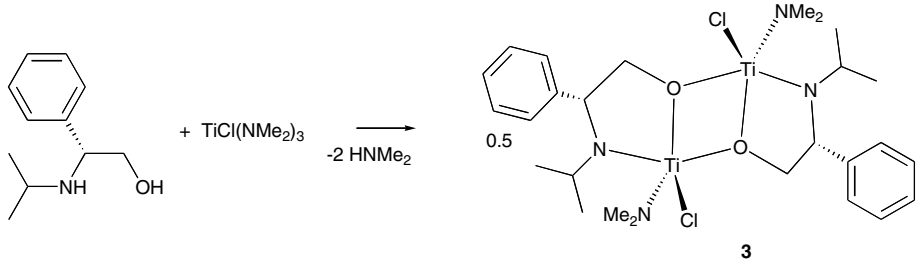
Fig. 1. Amino alcohol ligands used in this synthetic study.

The reaction of D-H_2PhgPrO with $TiCl(NMe_2)_3$ proceeds cleanly at room temperature over the course of several hours to form the dimeric species $[TiCl(NMe_2)$(D-PhgPrO)$]_2$ (**3**), Scheme 2. The proton NMR resonances for this complex are very similar to those reported for related amino alcohol complexes with titanium; four protons corresponding to the protons α to the heteroatoms appear in the region between 4.5 and 5.5 ppm. The solid state structure of complex **3** was determined by single crystal X-ray diffraction, and the gross structural features of the complex are very similar to those previously reported [33]. An ORTEP [41] and atom numbering scheme of complex **3** is shown in Fig. 2. Table 1 lists selected bond distances and angles for the metal coordination environment, while crystallographic data collection parameters and refinement statistics are listed in Table 2.

There are two molecules of **3** in the asymmetric unit; only one is shown for clarity. The two molecules are not equivalent, and the major difference between the two molecules is a rotation by about 20° of one of the phenyl rings (C16–C21) in one of the ligands. The ligand binds to titanium to form a five-membered metallocycle, and the amino alcohol oxygen bridges the two titanium centers. Each titanium has a highly distorted trigonal bipyramidal coordination environment. The two titanium-oxygen bond distances differ, with the Ti–O_{axial} (Ti1–O2 and Ti2–O1) bonds shorter by approximately 0.03 Å than the Ti–O_{eq} (Ti1–O1 and Ti2–O2) bonds. Each titanium center in the complex contains a terminal chloride and dimethylamide ligand. Each independent molecule is nearly twofold symmetric, with the rotation axis perpendicular to the Ti1–O1–Ti2–O2 heterocycle. The remaining bond distances and angles are unremarkable.

The $[TiCl(NMe_2)(L)]_2$ complexes are not very good catalysts for intramolecular hydroamination [42], although the structures of the active precatalysts are probably closely related. We therefore carefully monitored reactions of the free ligands with $Ti(NMe_2)_4$ while mimicking the reaction conditions of the catalytic reaction. Solutions of the ligand (any of a number of the amino alcohol ligands H_2L reported previously [32]) and the titanium starting material in C_6D_6 were mixed in J. Young NMR tubes. A color change occurred immediately upon mixing, and the formation of a single major (>90%) complex was observed spectroscopically. Attempts to purify the complex with any of the amino alcohol ligands have been hampered by the fact that all complexes are oils. Our assignment of the complex as $Ti(NMe_2)_3(HL)$ is based on the observation of three dimethylamide peaks in the region from 3.0 to 3.6 ppm that integrate to a total of 18 protons in the proton NMR spectrum.

Prolonged heating of the complex in the NMR tube at 100–100 °C for 12–18 h gives rise to a new complex $[Ti(NMe_2)_2(L)]_2$ with two sharp singlets each integrating to six protons at about 3.3 and 2.9 ppm due to the diastereotopic dimethylamide groups. The appearance of $HNMe_2$ at 2.3 ppm also confirms the proposed reaction. The dimeric nature of the complex is not known with certainty, but is postulated due to the similarity of the NMR resonances. Attempts to isolate the proposed complex were hampered by their non-crystallinity, except with the H_2PhgAdO ligand.



Scheme 2.

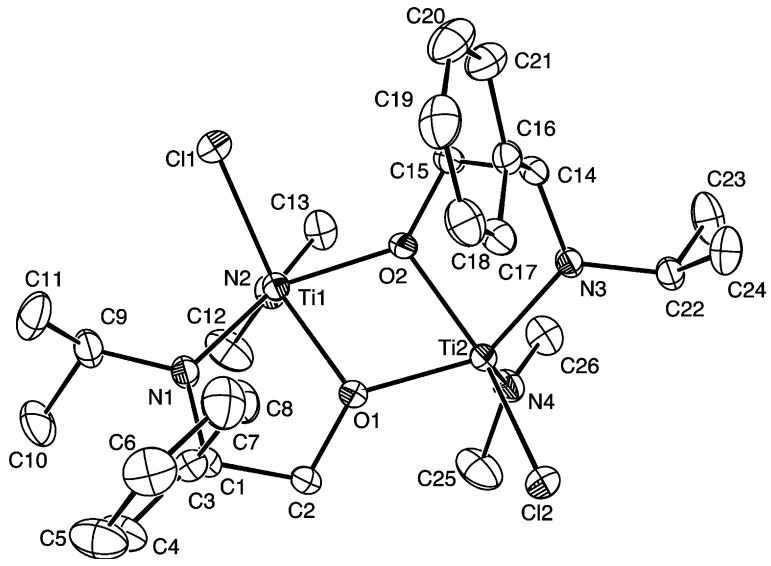


Fig. 2. ORTEP and partial atom numbering scheme for one of the two independent molecules of complex **3**. Ellipsoids are shown with 30% probability. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **3**

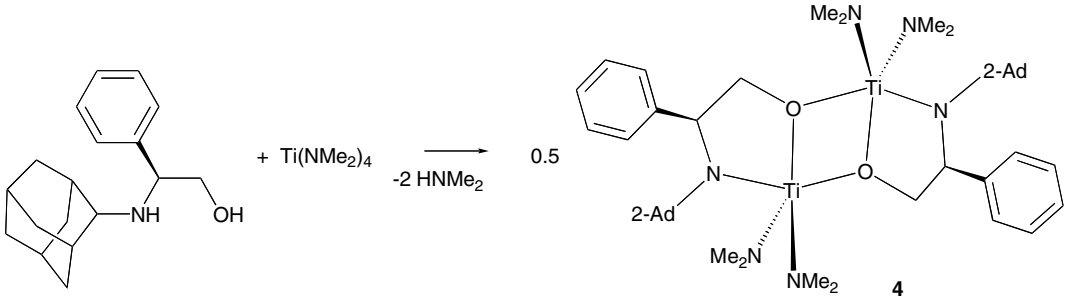
Ti1–O1	2.0337(15)	Ti2–O2	2.0190(15)
Ti1–O2	1.9943(15)	Ti2–O1	1.9958(15)
Ti1–N1	1.8927(18)	Ti2–N3	1.9039(17)
Ti1–Cl	2.3100(7)	Ti2–Cl2	2.3153(7)
Ti1–N2	1.8628(18)	Ti2–N4	1.8693(19)
N1–Ti1–N2	102.53(8)	N3–Ti2–N4	104.80(8)
N1–Ti1–O2	143.88(7)	N3–Ti2–O1	140.80(7)
N2–Ti1–O2	103.10(8)	N4–Ti2–O1	106.63(8)
N1–Ti1–O1	78.02(7)	N3–Ti2–O2	78.10(7)
N2–Ti1–O1	108.33(8)	N4–Ti2–O2	108.21(8)
O2–Ti1–O1	70.00(6)	O1–Ti2–O2	70.27(6)
N1–Ti1–Cl1	103.31(6)	N3–Ti2–Cl2	100.84(6)
N2–Ti1–Cl1	107.06(7)	N4–Ti2–Cl2	105.08(7)
O2–Ti1–Cl1	92.99(5)	O1–Ti2–Cl2	93.02(5)
O1–Ti1–Cl1	143.34(5)	O2–Ti2–Cl2	145.80(5)
Ti1–O1–Ti2	107.59(7)	Ti1–O2–Ti2	108.23(7)

A preparative scale reaction between L-H_2PhgAdo and $Ti(NMe_2)_4$ was carried out in toluene at 110 °C as shown in Scheme 3. After 18 h, the complex [$Ti(NMe_2)_2$(L-PhgAdO)]$_2$ (**4**) was isolated in 10% yield. The low yield is due to the extremely high solubility of the complex in all common solvents; the reaction is essentially quantitative by NMR spectroscopy. The complex exhibits two sharp singlets integrating to six protons at 3.325 and 2.890 ppm due to the diastereotopic dimethylamide groups, and there are four well spaced multiplets between 3.8 and 5.2 ppm due to the protons α to the heteroatoms in the ligand. The complex has resisted crystallization attempts to date and has only been isolated as fine microcrystals or as thin fibers that do not diffract sufficiently for structural determination.

Table 2
Crystallographic data collection parameters and refinement statistics for **3**

Empirical formula	$C_{26}H_{42}Cl_2N_4O_2Ti_2$
Formula weight	609.34
Color, habit	amber, block
Approximate crystal size (mm)	$0.20 \times 0.25 \times 0.25$
Crystal system	Monoclinic
Space group	*P*2(1)
a (Å)	13.7315(9)
b (Å)	13.5649(9)
c (Å)	17.1022(11)
β (°)	99.7130(10)
V (Å^3)	3139.9(4)
Z	4
T (°C)	213(2)
D_{calc} (g/cm^3)	1.289
F(0 0 0)	1280
Radiation	MoKα
μ (mm^{-1})	0.71073
Scan mode	*ϕ* and *ω*
θ Range (°)	1.76–28.20
Index ranges	$-18 \leqslant h \leqslant 18$
	$-18 \leqslant k \leqslant 18$
	$-21 \leqslant l \leqslant 22$
Total number of reflections	24,240
Number of unique reflections	12,901
Number of reflections with $I > 2\sigma$(I)	12,001
R_{int}	0.0235
Data/restraints/parameters	12,901/1/665
Final *R* indices [$I > 2\sigma(I)$]	0.0312
Weighted *R* [$I > 2\sigma(I)$]	0.0786
Goodness-of-fit	1.012
Residual density (eÅ^3)	−0.158, 0.376

Complex **4** is stable indefinitely at 100–110 °C and is presumably the active precatalyst for the hydroamination reaction. Importantly, it has two dimethylamide



Scheme 3.

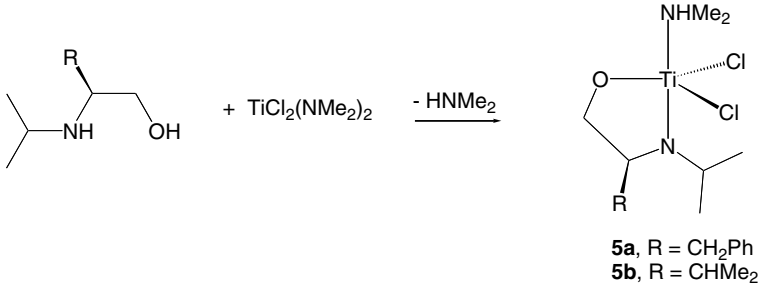
groups that can be substituted with the aminoallene to form the transient imido complex.

We postulated that the different reactivity between the amino alcohol ligands and $Ti(NMe_2)_4$, which requires extended heating for ligand replacement, and $TiCl(NMe_2)_3$, which is complete in a few hours, is due to an electronic effect. The presence of chlorine atoms on titanium increases the Lewis acidity of the metal, and thus the rate of reaction with the Lewis basic ligands. We therefore chose to examine the reactivity of $TiCl_2(NMe_2)_2$ with the amino alcohol ligands. There is a dramatic difference in reactivity with this starting material; a light brown product forms and precipitates immediately upon mixing etherial solutions of L-H_2Phe-PrO and $TiCl_2(NMe_2)_2$, as shown in Scheme 4. The complex that is isolated (complex **5a**) is extremely insoluble in non-polar solvents (benzene, hexane, ether) although it has limited solubility in toluene. The complex is quite soluble in thf and methylene chloride, but attempts to crystallize the complex from these solvents have been unsuccessful to date. Fortunately, the complex as isolated from the reaction mixture is analytically pure, and has the formula $TiCl_2(NHMe_2)$(L-PhePrO). The ability of Ti(IV) centers to tenaciously retain amine substituents has been reported previously [43].

The proton NMR spectrum of complex **5a** in toluene-d_8 exhibits extremely broad resonances at 20–25 °C. When the solution is heated, the broad resonances begin to coalesce to sharper signals, but the complex also decomposes to unknown products at temperatures around 50 °C. Upon cooling the solution to −5 °C, the resonances sharpen into clean signals. The spectrum at this temperature exhibits two resonances of equal intensity for each proton in the molecule. There is no further change in the spectra at lower temperatures.

The complex is so insoluble in toluene that accurate peak assignments could not be made, but the complex exhibits the same fluxional behavior at approximately the same temperatures in deuterated methylene chloride. Assignment of the proton NMR spectrum and confirmation of the molecular formula was aided with a heteronuclear COSY experiment. The complex has four inequivalent isopropyl methyl resonances appearing as doublets at 1.281, 1.386, 1.568 and 1.794 ppm. The two isopropyl methyne protons appear as clean and well-resolved septets at 6.063 and 6.402 ppm. The dimethylamine methyl resonances appear as doublets at 2.268, 2.632, 2.682 and 2.899 ppm. This splitting is due to the NH proton, confirming the structural assignment. The amine NH resonances appear as broad resonances, overlapping other peaks at 4.5 and 4.9 ppm. The two resonances for each proton in the molecule could be due to the presence of two inequivalent molecules with equal population at the lower temperature. However, based on the relatively high temperatures for coalescence, effectively ruling out simple pseudorotation [44,45], as well as the structure of the related complex **3**, we postulate that the dynamic behavior is due to a dimer/monomer equilibrium.

The complicated NMR spectrum and decomposition at elevated temperature have hampered our ability



5a, R = CH_2Ph
5b, R = $CHMe_2$

Scheme 4.

to fully simulate and interpret the dynamic behavior of the complex. We therefore prepared a derivative with simpler NMR signals by mixing L-H_2ValPrO with $TiCl_2(NMe_2)_2$ in ether (Scheme 4). A dark red–brown precipitate formed immediately, which was collected by filtration. Complex **5b** is significantly more soluble in ether than complex **5a**, and the yield of the complex is correspondingly lower. **5b** is also very soluble in thf and methylene chloride. The proton NMR spectrum of complex **5b** in CD_2Cl_2 exhibits broad resonances at 20–25 °C, again possibly indicating fluxional behavior. When the solution is heated, the broad resonances begin to coalesce to sharper signals, but the complex decomposes to unknown products at temperatures much above room temperature. Upon cooling the solution, the resonances begin to sharpen, and the low temperature limiting spectrum is at −25 °C. The spectrum at this temperature again exhibits two resonances of equal intensity for each proton in the molecule, and there is no further change in the spectra at lower temperatures.

Complex **5b** has eight inequivalent isopropyl methyl resonances appearing as doublets at 1.664, 1.421, 1.254, 1.132, 1.009, 0.954, 0.847, and 0.758 ppm. Two isopropyl methyne protons appear downfield as a broadened resonance at 6.3 ppm and the others are separated, but broad, at 4.7 and 4.3 ppm. The four dimethylamine methyl resonances appear as doublets at 2.789, 2.612, 2.420 and 2.396 ppm. The splitting of the *N*-methyl resonances by the NH proton confirms the presence of the coordinated amine. The amine NH resonances appear as broad resonances at 4.0 and 4.3 ppm.

Although complex **5b** was prepared in order to simplify the NMR signals for interpretation of the dynamic behavior, a full simulation and analysis has not yet been possible. Detailed interpretation of the NMR signals for **5b** is also hampered by its thermal instability.

4. Summary and conclusions

Titanium complexes with amino alcohol ligands have been previously shown to be effective catalysts for the intramolecular hydroamination of aminoallenes. In order to more fully understand the catalytically active species in the reaction, we investigated the synthesis of a variety of titanium complexes with these ligands. Most of the complexes have poor solubility and crystallinity behavior. We have prepared and purified three discrete titanium(IV) complexes with the general formulas $[Ti(L)(NMe_2)_2]_2$, $[Ti(L)(Cl)(NMe_2)]_2$ and $Ti(L)Cl_2$ with chiral amino alcohol ligands derived from phenylalanine, phenylglycine and valine. We are continuing our efforts to understand the coordination chemistry of titanium with these ligands. Studies are currently underway in order to trap a terminal imido complex starting from complex **4**. We are also continuing to model the dynamic behavior of complexes **5a** and **5b**.

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Appendix A. Supplementary data

CCDC 246787 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.09.051.

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