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Prolinol-Derived Phenoxy-Amidine Titanium Complexes in Asymmetric Silylcyanation of Aldehydes

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Pierre Le Gendre^{*[a]}

Three new tridentate phenoxy-amidine ligands (FA) have been prepared *via* the ring-opening of benzoxazole by 2-(methylamino)ethanol, *L*-prolinol and *L*-diphenylprolinol. Coordination studies of these FA ligands with Ti have led to the synthesis of the complexes (L1–L3)Ti(OⁱPr)₂ (**1 a–3 a**) and (L1–L3)TiCl₂(thf) (**1 b–3 b**). The solid state structures of the dichlorido FA–Ti complexes revealed a distorted octahedral geometry around the metallic centre provided by the FA ligand in *mer*-fashion, the two residual chloro ligands in *cis* arrangement and

a THF molecule. The chiral Ti-FA complexes were shown to promote the asymmetric silylcyanation reaction. With benzaldehyde as substrate, the best catalyst was the dichlorido Ti complex **3 b** with a diphenylprolinol in the ligand backbone. It afforded the cyanohydrine with 68% conversion and 74% ee after 24 h in DCM at –20 °C. The diisopropoxy Ti complex **3 a** was remarkably active with pivalaldehyde as substrate, yielding the cyanosilylated product with 99% conversion and 61% ee after only 30 min at –60 °C.

Introduction

The coordination chemistry of amidinates has been fully studied and is well documented.^[1] Much less is known about amidines in this respect.^[2] However, amidines, which can be considered as $2\sigma,2\pi$ -electron donors, are also potentially suitable ligands for the stabilization of electron-deficient metal ions. Furthermore, the fact that amidines, like DBU or DBN, are commonly used as bases in organic synthesis suggests that they are rather robust, which is an advantage for their use as ligands.^[3] With this in mind, we recently turned our attention toward new families of bidentate [N,O[–]] ligands combining a phenoxy group and an *N,N,N'*-trisubstituted amidine moiety.^[4] These new variants of phenoxy-imine ligands (FI) have been shown to form stable chelate complexes with oxophilic metals such as Zn and Al. Some of these complexes were shown to promote the Ring Opening Polymerization of lactide (ROP) even in the presence of lactic acid (an impurity often present in technical grade monomer), contrary to the parent phenoxy-imine complexes.^[4b] In parallel, we developed a tetradentate version of these ligands as an analogous of the ubiquitous salen ligands by combining two phenoxy-amidine moieties.^[5] These ligands, named FALen,

showed unique coordination chemistry compared to salen, being able to adapt their denticity depending on the electron richness of the metal ion. With the aim to extend further the scope of phenoxy-amidine ligands (FA) and gain insights into the coordination of amidines, we endeavor to develop a chiral tridentate [O,N,O] version of FA. Since the pioneering works of Noyori,^[6] chiral Schiff base ligands have been intensively used in asymmetric catalysis and afford among the most versatile and performant systems.^[7] The chiral tridentate [O,N,O] Schiff base and their Ti complexes, to name a few, were shown able to promote a wide array of asymmetric transformations such as the silylcyanation of aldehydes and imines,^[8] the addition of diketene to aldehydes,^[9] the aldol reaction,^[10] the hetero Diels Alder reaction,^[11] the oxidation of *t*-Bu-disulfide^[12] or the hydroamination of olefines.^[13] Here we report on the synthesis of new tridentate [O,N,O] FA ligands, two of which are derived from prolinol, along with their coordination chemistry with Ti and preliminary assessment as catalysts in the asymmetric silylcyanation of aldehydes.

Results and Discussion

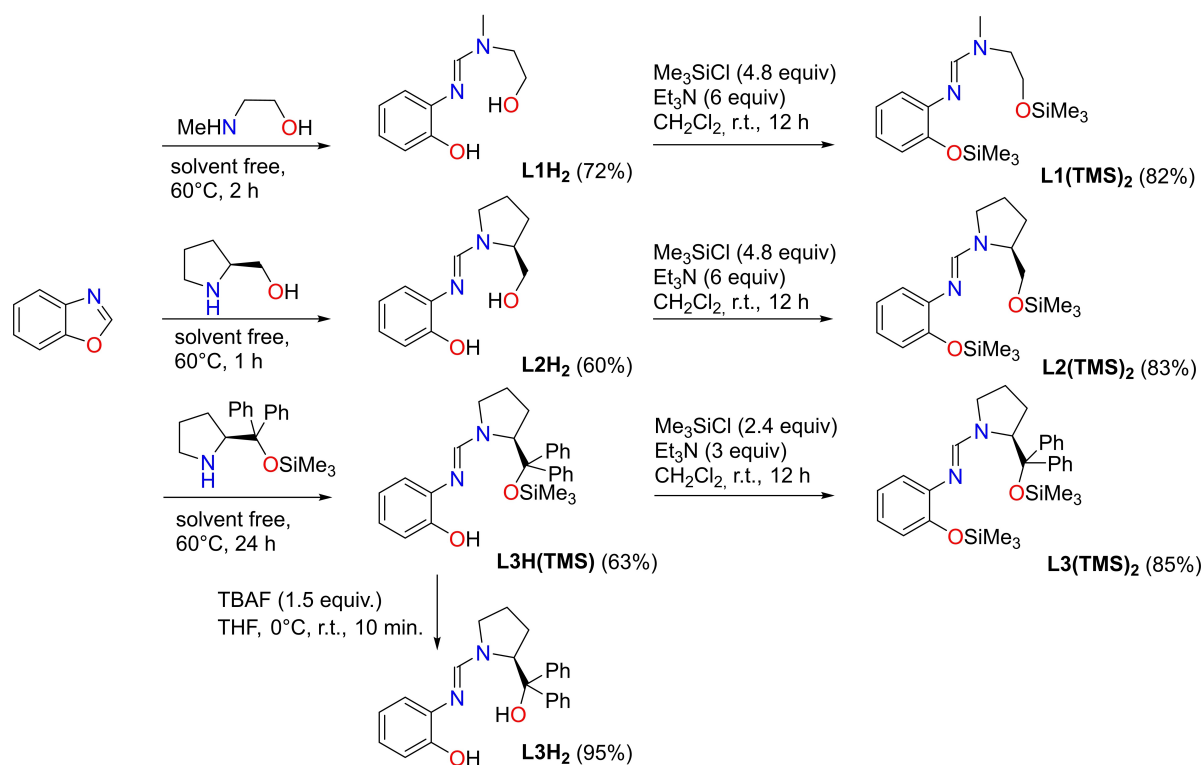
Synthesis of the Proligands

The prolignands **L1H₂** and **L2H₂** were readily prepared through the ring opening of benzoxazole by 2-(methylamino)ethanol and *L*-prolinol, respectively, in solvent-free condition at 60 °C for 1–2 h (Scheme 1).^[14] Reaction of benzoxazole with diphenylprolinol, which is solid, was more challenging in solvent-free conditions and resulted in incomplete conversion after 18 h at 80 °C. Furthermore, the use of solvents such as toluene to solubilize the compounds and promote reaction proved unsuccessful. We therefore synthesized diphenylprolinol trimethylsilyl ether, which is in oil form and hence more suitable for

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Scheme 1. Synthesis of the proligands.

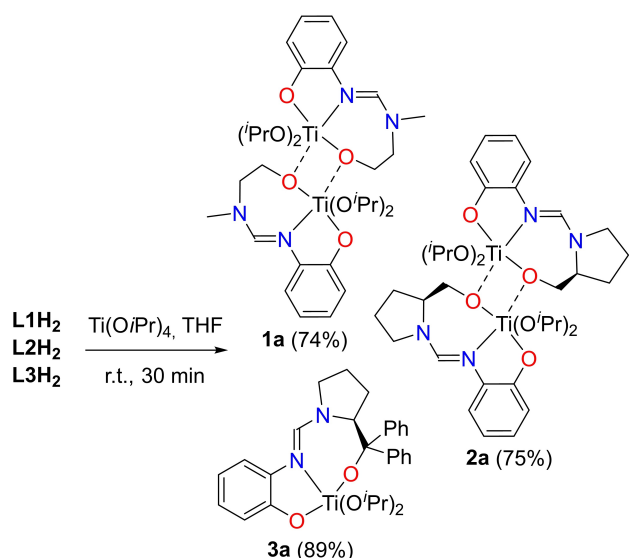
solvent-free reactions. The benzoxazole opening product L3H(TMS) was thus obtained in 63% yield. Deprotection of the TMS group using TBAF in THF for 10 min gave the proligand in its diprotonated form (L3H₂) in 95% yield. Finally, bis(silylether) versions of the three FA ligands were also synthesized. ¹H NMR spectra in CD₂Cl₂ at 298 K of the proligands L1H₂, L1(TMS)₂ and L2H₂ show broad signals with a splitting notably of the amidine proton signals into two sets of signals of unequal intensity. The VT NMR experiment conducted on L2H₂ in CDCl₃ showed coalescence to give an average spectrum at 310 K (see SI, Figure S13). This NMR behavior can be attributed to a restricted rotation around the amidine C-NRR' bond. It should be noted that the spectra become simpler in MeOD, suggesting a faster interconversion of the rotamers in this solvent. The NMR spectra of the prolinol-derived proligands {L3H₂, L2(TMS)₂, L3(TMS)₂} showed only one set of resonances at 298 K both either in CD₂Cl₂ or in MeOD.

Synthesis of the FA-Ti Complexes

The titanium Schiff base complexes used in asymmetric silylcyanation reactions are most often generated in situ from titanium isopropoxide and the appropriate Schiff base ligand.^[15] Efforts to identify the complexes formed under these conditions showed that, in the absence of the ortho-ⁱBu substituent in the Schiff base, the active species [L*Ti(OⁱPr)₂] formed together with an inactive homoleptic complex [L*₂Ti].^[16] This contributes to lower enantiomeric excesses due to the presence of residual

Ti(OⁱPr)₄, which can promote the silylcyanation reaction in a non-stereoselective manner. Consequently, our approach was first to ensure that FA diisopropoxy titanium complexes could be formed selectively from tridentate FA ligands, and then test their catalytic ability. In addition, we sought to synthesize a dichlorido version of these complexes in order to study the impact it might have on catalysis.

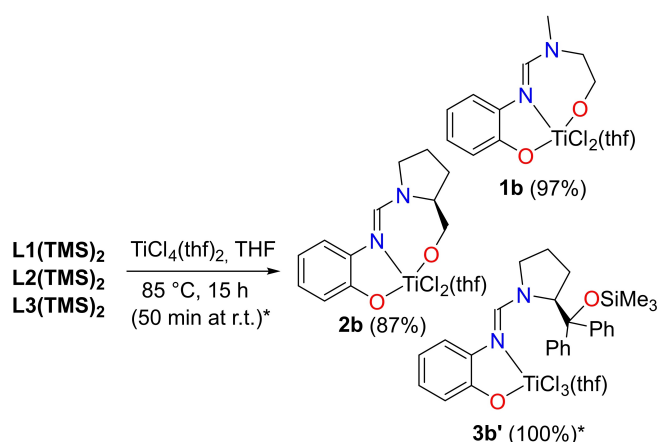
The reaction of the proligands L1H₂–L3H₂, with one equivalent of Ti(OⁱPr)₄ resulted in the formation of the corresponding diisopropoxy complexes 1a–3a as single products in 74–89% yields (Scheme 2). The ¹H NMR spectra of compounds 2a and 3a in TDF showed only one singlet for the formamidine proton at 7.96 ppm and 8.23 ppm, respectively. The chirality of these complexes was notably reflected in the diastereotopic splitting of the signal of the isopropoxy methyls, which appear as four doublets between 0.88 and 1.40 ppm. Complex 1a showed an NMR spectrum at 298 K similar to that of complexes 2a and 3a, but with much broader signals. Variable temperature ¹H NMR experiments conducted on complex 1a reveal isopropoxy-methyl signals as four distinct doublets at temperatures below 273 K and a single broad signal at temperatures above 313 K (See SI, Figure S44). We hypothesized that this NMR behaviour is due to the fact that 1a has a dimeric structure in solution, which tends to split with increasing temperature. DOSY measurements of 1a using tris(trimethylsilyl)silane (TTMSS) as an internal reference showed that 1a exists mainly as a dimer in TDF solution at 298 K (See SI, Figure S55). X-ray analysis of a single crystal of 1a also showed a dimeric structure, although the data quality did not allow



Scheme 2. Synthesis of the FA-Ti(OiPr)₂ complexes.

further discussion of structural parameters (See SI, Figure S82). It should also be mentioned that DOSY experiments on **2a** and **3a** supported a dimeric structure in solution for the former and a monomeric structure for the latter (See SI, Figures S56 and S57). The first synthetic route we investigated to access the dichlorido complexes **1b–3b** involved the reaction of the proligands L1H₂–L3H₂ with the precursor TiCl₄(thf)₂ in the presence of triethylamine.^[17] The desired complexes formed under these conditions, but were contaminated by the triethylammonium salt, which we were unable to remove despite numerous attempts.

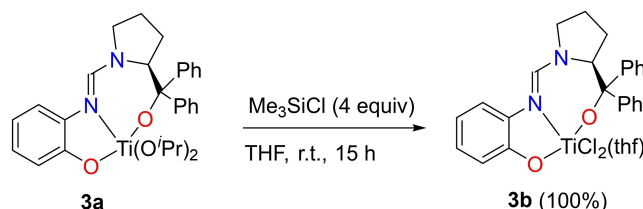
A salt metathesis route involving the addition of the phenoxy-amidine alcoholate disodium salts to TiCl₄(thf)₂ also failed in our hands.^[18] In contrast, the reaction of the silylated proligands L1(TMS)₂ and L2(TMS)₂ with TiCl₄(thf)₂ in THF at 85 °C overnight afforded complexes **1b** and **2b** in 97% and 87%, yields, respectively (Scheme 3).^[19] When the proligand L3(TMS)₂ was used under the same conditions, only one of the silyl ether functions reacted, yielding the κ^[2]-coordinated FA Ti



Scheme 3. Synthesis of the FA-TiCl_n(thf) complexes **1b**, **2b** and **3b**.*

complex **3b**' with a pendant silyl ether. The latter could be obtained with a quantitative yield after only 50 minutes at room temperature. The dichlorido complex **3b** could be obtained alternatively through the addition of Me₃SiCl to the diisopropoxy complex **3a** (Scheme 4).^[20] Single crystal X-ray analysis of complexes **1b–3b** revealed that the Ti atom is in pseudo-octahedral geometry, chelated by the FA ligand in tridentate [O,N,O] form and in a *mer* configuration with both oxygen atoms in *trans* position (Figure 1). The coordination sphere of Ti is completed by a THF molecule, and two chlorine atoms in a *cis* position. The three complexes exhibited comparable twisted conformations of the seven-membered N,O metallacycles, with the amidine moiety slightly tilted with respect to the metal chelation plane.

Complex **1b** has two different molecules in the unit cell, distinguished by the position of the THF ligand (and apical Cl⁻), relatively up or down the coordination plane. In complexes **2b**



Scheme 4. Synthesis of the FA-TiCl₂(thf) complex **3b**.

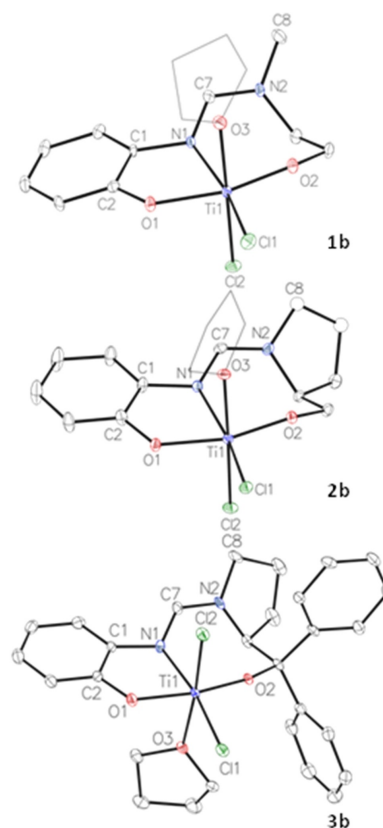


Figure 1. Views of complexes **1b–3b** (ORTEP, 50% probability ellipsoids; H atoms as well as the second independent molecule for **1b** are omitted for clarity). For relevant bond distances and angles, see Table 1.

and **3b**, the THF ligand is not located on the same side of the metal coordination plane.

Complexes **1b** and **2b** displayed slightly negative Δ_{CN} values ($\Delta_{\text{CN}} = d_{\text{N2C7}} - d_{\text{N1C7}}$) and longer Ti–Cl1 bond than Ti–Cl2 bond probably due to the *trans* influence of the amidine function (Table 1). In comparison, electron delocalization appeared to be little less pronounced in **3b** ($\Delta_{\text{CN}} = 0.014(7)$), and the Ti–Cl1 bond was shorter than the Ti–Cl2 bond. ^1H NMR of complexes **1b–3b** showed the presence of a single isomer in solution, with the characteristic downfield shifted signal of the formamidine appearing as a singlet at 7.93, 8.11 and 8.23 ppm, respectively.

Enantioselective Silylcyanation of Benzaldehyde and Pivalaldehyde

The titanium complexes were further studied as catalysts in asymmetric cyanosilylation of aldehydes. The reactions were conducted at room temperature using benzaldehyde and trimethylsilyl cyanide in 1:2 ratio in dichloromethane (TMSCN, 1 M) using 5 mol% of catalyst (Table 2). The reaction conversions have been determined by ^1H NMR. After hydrolysis of the silyl ether, the cyanohydrin has been reacted with acetic anhydride to give the corresponding cyano acetate which was analyzed by chiral GC. Alkoxy-titanium complexes **1a** and **2a** showed moderate activity in cyanosilylation, yielding 83 and 93% conversion after 24 h (entries 1 and 2, Table 2). In comparison, complex **3a** showed higher activity, reaching full conversion after 1 h (entry 3) under the same conditions. Complex **2a** gave an enantioselectivity of 16% in favour of the (S) enantiomer (entry 2). Interestingly, complex **3a** with the

Table 1. Relevant bond distances (Å) and angles (°) in complexes **1b–3b**.

	Ti–O1	Ti–O2	Ti–N1	Ti–Cl1	Ti–Cl2	$\Delta_{\text{CN}}^{[a]}$	$\psi^{[b]}$
1b ^[c]	1.911(2)	1.787(2)	2.175(12)	2.342(13)	2.324(7)	−0.011(7)	−154(6)
2b	1.907(4)	1.799(4)	2.178(5)	2.3341(18)	2.3201(18)	−0.015(11)	−163.8(6)
3b	1.906(3)	1.791(2)	2.178(3)	2.3254(10)	2.3494(10)	0.014(7)	−152.1(3)

^[a] $\Delta_{\text{CN}} = d_{\text{N2C7}} - d_{\text{N1C7}}$. ^[b] ψ (C7 N1 C1 C2). ^[c] The mean values of the two independent molecules are reported.

Table 2. Aldehydes cyanosilylation with FA Ti complexes.^[a]

Entry	Aldehyde	Cat.	T(°C)	Time	Conv (%) ^[b]	ee (%) ^[c,d]
1	PhCHO	1a	25	24 h	83	–
2	PhCHO	2a	25	24 h	93	16 (S)
3	PhCHO	3a	25	1 h	100(100) ^[e]	31(29) ^[e] (R)
4	PhCHO	1b	25	140 h	100	–
5	PhCHO	2b	25	140 h	98	8 (S)
6	PhCHO	3b	25	3 h	93	67 (R)
7	PhCHO	3a	−20	1 h	96(99) ^[e]	56(46) ^[e] (R)
8	PhCHO	3a	−60	5.5 h	89	65 (R)
9	PhCHO	3b	−20	24 h	68	74 (R)
10	PhCHO	3b'	25	1 h	98	10 (S)
11 ^[f]	PhCHO	L3H₂/Ti	25	3 h	100	16 (R)
12	^t BuCHO	3a	25	5 min	100	34 (R)
13	^t BuCHO	3a	−20	10 min	100	53 (R)
14	^t BuCHO	3a	−60	30 min	99	61 (R)
15	^t BuCHO	3b	25	6 h	100	13 (R)
16	^t BuCHO	3b	−20	14 h	95	38 (R)

^[a] Conditions: TMSCN/RCHO/[Ti] = 2/1/0.05, [TMSCN] = 1 M, CH₂Cl₂. ^[b] Determined by ^1H NMR. ^[c] Determined by chiral GC analysis. ^[d] The absolute configurations were determined by measurement of the optical rotation and comparison with the literature. ^[e] Reaction performed using *in situ* generated catalyst from **L3H₂/Ti(OⁱPr)₄** = 1/1. ^[f] Reaction performed using *in situ* generated catalyst from **L3H₂/Ti(O-*n*-Bu)₄/H₂O** = 1/1/0.75.

diphenylprolinol-derived FA ligand gave the opposite enantiomer (*R*) with a higher ee of 31% (entry 3). The dichlorido Ti complexes (**1b–3b**) showed similar trends but proved less active than their isopropoxy counterparts (entries 4–6). Conversely regarding enantioselectivity, the use of the dichlorido complex **3b** instead of the diisopropoxy complex **3a** resulted in a significant increase in the enantiomeric excess (ee = 67% vs 31%, entries 6 vs 3). Enantioselectivity was further improved by performing the silylcyanation reaction at lower temperatures. Reactions at -20°C with **3a** gave 56% ee, while with **3b** ee reached 74% (entries 7 and 9). Nevertheless, the latter required 24 h reaction time to compensate for the decreased activity. Reducing the temperature to -60°C additionally enhanced ee up to 65% with **3a** (entry 8). The silylcyanation reaction using [L3(TMS)- $\kappa\text{N},\kappa\text{O}$]TiCl₃(thf) (**3b'**) was faster compared to that with **3b**. However, it resulted in a lower ee (entries 10 vs 6). As mentioned above, the titanium Schiff base complexes used in asymmetric silylcyanation reactions are most often generated *in situ*. Catalytic tests using a combination of L3H₂ with Ti(O^{*i*}Pr)₄ gave similar activity to **3a** but led to a slightly lower enantiomeric excess at -20°C (entries 3 and 7). In contrast to what had been observed with Schiff base ligands, the combination of L3H₂ with a partially hydrolyzed Ti *n*-butoxide did not improve the kinetic and/or the stereoselectivity of the cyanosilylation reaction (entry 11 vs entry 3).^[21]

If we compare the performance of catalysts **2a** and **3a** with that generated *in situ* from Ti(O^{*i*}Pr)₄ and Schiff base ligands derived from *L*-valinol, it appears that the former exhibit higher activity, but lead to lower enantiomeric excesses.^[8a,b] Interestingly, Oguni shown that the use of Schiff base ligand derived from 1,1-diphenylvalinol instead of valinol also resulted in improved and opposite enantioselectivity. A comparison with catalysts generated *in situ* from camphor-derived Schiff bases and Ti(O^{*i*}Pr)₄ revealed also enhanced activity for FA–Ti complexes and lower enantioselectivities (74–86%, 8–81% ee, -20°C , 48 h, CH₂Cl₂, [Ti(O^{*i*}Pr)₄-camphor derived Schiff's bases] = 20 mol%).^[16b] To the best of our knowledge, the combination of TiCl₄ and a Schiff base ligand for asymmetric silylcyanation has not been reported, which prevents a direct comparison with complexes **2b** and **3b**. Nevertheless, it is worth mentioning that the highest ee value obtained with **3b** at -20°C is slightly lower than those reported with the best tridentate Schiff base ligands.^[8,15,16] These catalysts do not compare, however, with the bis(salen)ditanium complexes previously reported by Ding for this reaction.^[22] In the reaction model proposed by Oguni, the ^{*t*}Bu group on the aryloxy moiety is critical to enantioselectivity by blocking the *Re* face of the coordinated aldehyde. Our assumption is that, in case of complex **3b**, the benzaldehyde replaces the thf ligand on Ti and that is one of the two phenyl groups at the C1 position of prolinol that blocks the *Re* face (Figure 2).

To confirm this, we computationally studied the stability of all rotamers obtained by coordinating a benzaldehyde molecule to the L2TiCl₂ and L3TiCl₂ complexes. The most stable isomers are reported on Figure 2. As expected, for L3TiCl₂(PhCHO) the most stable conformer resembles the model proposed by Oguni with a shallow H-bond between the aldehyde and the chlorine

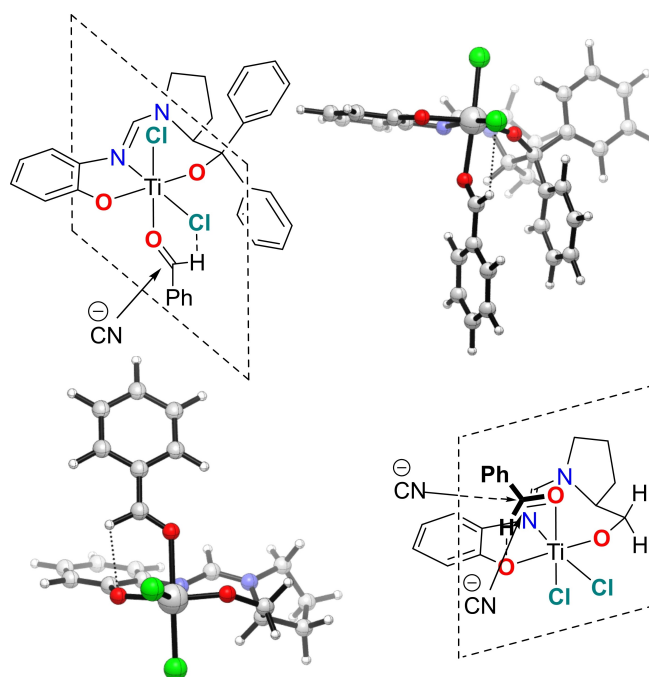


Figure 2. Most stable rotamers of benzaldehyde adducts with complexes **3b** (top) and **2b** (bottom).

atom linked to the metal. The isomer leading to the attack to the *Re* face is located 1.8 kcal/mol above this one and will thus contribute much less to the reaction (see Figure S87).

For L2TiCl₂(PhCHO) the most stable isomer (Figure 2) can lead to the attack on both faces of benzaldehyde. This result could explain both the opposite enantioselectivity and the low enantiomeric excess observed when using **2b** vs **3b** in the asymmetric silylcyanation reaction.

The asymmetric cyanosilylation was further investigated with pivalaldehyde using complexes **3a** and **3b**. The reaction performed in the presence of 5 mol% of complex **3a** was much faster than for benzaldehyde, giving 100% conversion after only 5 min at 25°C against 1 h for PhCHO (entries 12 vs 3). At -20°C , the reaction was completed within 10 min and reached 99% conversion at -60°C in only 30 min. Lowering the reaction temperature also had a favourable effect on the enantiomeric excess, with values of 34% at 25°C , 53% at -20°C , and 61% at -60°C (entries 12–14). In comparison, the complex *in situ* generated from Ti(O^{*i*}Pr)₄ and the Schiff base ligand derived from *L*-valinol and 3-*tert*-butyl-2-hydroxybenzaldehyde afforded the cyanohydrin in 58% yield and 70% ee after 36 h at -80°C , employing 20 mol% catalyst loading.^[8b] Complex **3b** was much less active for the silylcyanation of pivalaldehyde, giving a total conversion after 6 h at 25°C and 95% conversion after 14 h at -20°C (entry 15). Complex **3b** gave rise also to lower enantioselectivities than **3a** for the silylcyanation of pivalaldehyde with ee value reaching 38% at -20°C (entry 16).

Conclusions

We have developed a new class of tridentate FA ligands derived from 2-(methylamino)ethanol, *L*-prolinol and *L*-diphenylprolinol. Subsequent complexation of these ligands with $\text{Ti}(\text{O}^i\text{Pr})_4$ resulted in the formation of $(\text{L}1\text{--}\text{L}3)\text{Ti}(\text{O}^i\text{Pr})_2$ complexes (**1a–3a**). These complexes do not undergo a redistribution process that leads to the corresponding homoleptic compounds and $\text{Ti}(\text{O}^i\text{Pr})_4$, as previously observed with the parent tridentate Schiff base ligands. Dichlorido complexes $(\text{L}1\text{--}\text{L}3)\text{TiCl}_2(\text{thf})$ (**1b–3b**) have also been prepared. X-ray analysis revealed that the FA ligands are coordinated in a *mer*-fashion, with residual thf molecule coordinated either above or below the coordination plane depending on the ligand backbone. The optimal catalyst for the silylcyanation of benzaldehyde proved to be the dichlorido Ti complex **3b** bearing FA ligand derived from *L*-diphenylprolinol. This complex gave an enantioselectivity of 74% at -20°C , surpassing that of diisopropoxy complex **3a**. With pivalaldehyde as substrate, complex **3a** was the best, giving honorable enantioselectivity ($ee=61\%$ at -60°C) and impressive activity ($\text{TOF}\approx 40\text{ h}^{-1}$), compared to complex **3b** ($\text{TOF}\approx 1\text{ h}^{-1}$ at -20°C) and to other benchmark tridentate Schiff base titanium complexes.^[8,15,23] Further optimizations of these prolinol-derived FA ligands, including the introduction of bulky substituents at the ortho position of the aryloxy moiety, are currently underway.

Experimental Section

All reactions, except when indicated, were carried out under an atmosphere of argon using conventional Schlenk techniques and Ar glovebox. DCM, diethyl ether, THF, toluene, and pentane were dried using a MBRAUN SPS 800. Analyses were performed at the "Plateforme d'Analyses Chimiques de Synthèse Moléculaire de l'Université de Bourgogne". Elemental analyses were performed by Ms Tiffanie Régnier on CHNS ThermoFisher Scientific Flash EA 1112 analyser. Reagents were commercially available and used as received. High resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL ESI-MS (ElectroSpray Ionization Mass Spectrometry). All X-Ray experimental data procedure and refinement are detailed in Supplementary Information.^[24] NMR spectra (^1H , ^{13}C) were recorded on Bruker 400 Avance Neo, Bruker 500 Avance Neo, or Bruker 600 Avance HD spectrometers. Chemical shifts are quoted in parts per million (δ) relative to TMS (for ^1H and ^{13}C). For ^1H and ^{13}C spectra, values were determined by using solvent residual signals (e.g. CHCl_3 in CDCl_3) as internal standards. The apparent multiplicity of the ^1H signals is reported. Assignment of ^1H and ^{13}C signals (when possible) was done through the use of 2D experiences (COSY, HSQC and HMBC). Nomenclature: the positions of carbon and hydrogen atoms in FA ligands were labelled according to Figure 3.

The enantiomeric excess of the acetate derivative was determined by GC, using GC-2010 Shimadzu device equipped with a chiral β -DEX 120 column (30 m \times 0.25 mm). Method: Column flow = 1.19 mL/min (N_2); Split = 1. Gradient: 60°C for 2 min, then $10^\circ\text{C}/\text{min}$ up to 200°C , then 200°C for 5 min. Specific rotation was determined with an Anton Paar MCP device with a 100 mm long cell at 20°C and at 589 nm. Measures were conducted in CHCl_3 .

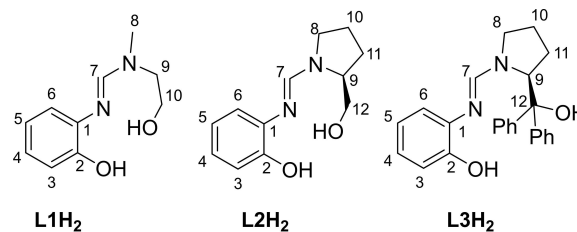


Figure 3. Numbering of C/H atoms in FA ligands.

Synthesis of L1H₂

Benzoxazole (1.07 g, 9 mmol) and 2-hydroxy-*N*-methylethylamine (1.2 mL, 15 mmol, 1.7 equiv) were heated under stirring at 60°C for 2 h. The crude product was then recrystallized from hot AcOEt, filtrated and dried under vacuum to afford 967 mg of pure **L1H₂**. The filtrate was concentrated by evaporation and a second batch of crystals was isolated by filtration and dried under vacuum to give 300 additional mg of **L1H₂** (72% yield). $^1\text{H NMR}$ (400 MHz, MeOD, **298 K**): $\delta(\text{ppm})=7.75$ (broad signal, 1H, H7), 6.92–6.81 (overlapping signals, 2H, H4+H6), 6.77 (d, $J=7.2\text{ Hz}$, 1H, H3), 6.72 (t, $J=7.5\text{ Hz}$, 1H, H5), 3.91–3.33 (overlapping broad signals, 4H, H9+H10), 3.06 (broad signal ($\Delta\nu_{1/2}=10.2\text{ Hz}$), 3H, H8). $\{^1\text{H}\}^{13}\text{C NMR}$ (101 MHz, MeOD, **298 K**): $\delta(\text{ppm})=156.17$ (C7), 151.43 (C2), 139.54 (C1), 124.57 (C6), 120.84 (C5), 119.99 (C4), 115.21 (C3), 60.28 (C10), 56.63 (C9), 33.26 (C8). **Elemental analysis**: calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.72; H, 7.27; N, 14.24. **HR-MS (ESI-pos)**: calcd for $[\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2]^+$ [M+H] $^+$: 195.11280. Found: 195.11198 (-4.203 ppm).

Synthesis of L2H₂

Benzoxazole (1.07 g, 9 mmol) and *L*-prolinol (1.3 mL, 13.5 mmol, 1.5 equiv) were heated at 60°C for 1 h. The crude product was then recrystallized from hot AcOEt to afford 1.18 g of **L2H₂** (60% yield). $^1\text{H NMR}$ (600 MHz, MeOD, **298 K**): $\delta(\text{ppm})=8.04$ (s, 1H, H7), 6.89 (d, $J=7.8\text{ Hz}$, 1H, H6), 6.85 (t, $J=7.5\text{ Hz}$, 1H, H5), 6.77 (d, $J=8.0\text{ Hz}$, 1H, H3), 6.71 (t, $J=7.5\text{ Hz}$, 1H, H4), 3.86 (broad signal ($\Delta\nu_{1/2}=40.4\text{ Hz}$), 1H, H8) 3.76–3.46 (overlapping signals, 4H, H9+H8+H12), 2.18–1.87 (overlapping signals, 3H, H10+H11), 1.82 (m, 1H, H10). $\{^1\text{H}\}^{13}\text{C NMR}$ (150 MHz, MeOD, **298 K**): $\delta(\text{ppm})=153.45$ (C7), 151.75 (C2), 139.31 (C1), 124.81 (C5), 120.65 (C4), 120.32 (C6), 115.66 (C3), 65.57 (C12), 62.78 (C9), 46.94 (C8), 28.48 (C10/C11), 24.12 (C10/C11). **Elemental analysis**: calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.10; H, 7.19; N, 13.12. **HR-MS (ESI-pos)**: calcd for $[\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_2]^+$ [M+H] $^+$: 221.12845. Found: 221.12748 (-4.387 ppm). $[\alpha]_D^{20} = +16.3$ ($c=0.42$, CHCl_3).

Synthesis of L3H(TMS)

425 mg (1.32 mmol) of (*S*)-1,1-diphenylprolinol trimethylsilyl ether^[25] and 310 mg (2.60 mmol, 2 equiv) of benzoxazole were stirred at 60°C for 24 h. The crude solid was then purified by column chromatography on silica gel using a mixture of PE/AcOEt (10/2 and then 10/5) as eluent, affording 370 mg of **L3H(TMS)** as a beige solid (63% yield). $^1\text{H NMR}$ (400 MHz, CD_2Cl_2 , **298 K**): $\delta(\text{ppm})=8.10$ (s, 1H, H7), 7.48–7.31 (overlapping signals, 10H, 2xAr), 6.86 (td, $J=7.5, 1.6\text{ Hz}$, 1H, H4), 6.81 (dd, $J=7.8, 1.6\text{ Hz}$, 1H, H3), 6.78 (d, $J=7.3\text{ Hz}$, 1H, H6), 6.72 (td, $J=7.5, 1.6\text{ Hz}$, 1H, H5) 4.80 (dd, $J=9.0, 1.8\text{ Hz}$, 1H, H9), 3.49 (m, 1H, H8), 2.57 (m, 1H, H8), 2.23 (m, 1H, H11), 2.01 (m, 1H, H11), 1.56 (m, 1H, H10), 0.94 (m, 1H, H10), -0.19 (s, 9H, SiMe_3).

$\{^1\text{H}\}^{13}\text{C}$ NMR (101 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 151.76$ (C7), 150.71 (C2), 142.67 (Ar), 142.39 (Ar), 137.99 (C1), 129.90 (Ar), 129.82 (Ar), 128.45 (Ar), 128.39 (Ar), 128.12 (Ar), 127.90 (Ar), 123.40 (C4), 119.83 (C5), 115.47 (C6), 113.19 (C3), 84.37 (C12), 68.93 (C9), 47.14 (C8), 28.13 (C11), 22.60 (C10), 1.88 (SiMe_3). **Elemental analysis:** calcd for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_2\text{Si}$: C, 72.93; H, 7.25; N, 6.30. Found: C, 72.63; H, 6.58; N, 6.20. $[\alpha]_D^{20} = -263.0$ ($c = 0.37$, CHCl_3).

Synthesis of L3H₂

Under argon, 3 g (6.75 mmol) of L3H(TMS) were solubilized into 150 mL of dried THF. The solution was cooled to 0 °C and 10.1 mL (10.12 mmol, 1.5 equiv) of a 1 M solution of TBAF in THF were added dropwise. The solution was allowed to reach r.t. and the volatiles were evaporated. The product was taken back into 300 mL of CH_2Cl_2 and hydrolyzed with 45 mL of distilled water. The phases were separated and the product was further extracted with 2×150 mL of CH_2Cl_2 . The organic phases were combined, dried over MgSO_4 and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using EtOAc as eluent to afford 2.4 g of L3H₂ (95% yield). ^1H NMR (500 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 7.59$ –7.45 (overlapping signals, 4H, Ar), 7.45–7.34 (overlapping signals, 4H, Ar), 7.34–7.25 (overlapping signals, 3H, Ar + H7), 6.85 (t, $J = 7.6$ Hz, 1H, H4/H5), 6.79 (dd, $J = 8.0$, 1.5 Hz, 1H, H3/H6), 6.65 (broad signal, 1H, H4/H5), 6.27 (broad signal, 1H, H3/H6), 4.86 (broad signal ($\Delta\nu_{1/2} = 21.0$ Hz), 1H, H9), 3.70 (broad signal ($\Delta\nu_{1/2} = 29.0$ Hz), 1H, H8), 3.39 (broad signal ($\Delta\nu_{1/2} = 33.1$ Hz), 1H, H8), 2.18 (m, 1H, H11), 2.04 (m, 1H, H11), 1.78 (broad signal, 2H, H10). $\{^1\text{H}\}^{13}\text{C}$ NMR (125 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 152.25$ (C7), 150.41 (C2), 145.84 (Ar), 144.84 (Ar), 137.33 (C1), 128.87 (Ar), 128.58 (Ar), 127.77 (Ar), 127.68 (Ar), 127.10 (2xAr), 123.96 (C4/C5), 120.03 (C4/C5), 115.99 (C3/C6), 113.56 (C3/C6), 81.34 (C12), 68.09 (C9), 48.34 (C8), 29.22 (C11), 23.77 (C10). **Elemental analysis:** calcd for $(\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2)_{100}(\text{C}_4\text{H}_8\text{O}_2)_7$: C, 76.73; H, 6.89; N, 7.37. Found: C, 76.51; H, 6.91; N, 7.35. $[\alpha]_D^{20} = -225.6$ ($c = 0.32$, CHCl_3).

Synthesis of L1(TMS)₂

Under argon, 587 mg (3.0 mmol) of L1H₂ were solubilized in 20 mL of dry CH_2Cl_2 . 2.5 mL (18 mmol, 6 equiv) of triethylamine were added and the solution was cooled at 0 °C. TMSCl (1.8 mL, 14.4 mmol, 4.8 equiv) was added dropwise and the mixture was then allowed to reach room temperature and stirred overnight. The volatiles were evaporated under vacuum and the crude product was extracted with 15 mL then 2×10 mL of dry diethyl ether *via* a filtrating cannula. The filtrate was evaporated under vacuum affording 829 mg of L1(TMS)₂ as a mixture of two isomers A and B in a 1/0.5 ratio (82% yield). ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): *Isomer A*: $\delta(\text{ppm}) = 7.53$ (s, 1H, H7), 6.89–6.75 (overlapping signals, 4H, H3 + H4 + H5 + H6), 3.70 (broad signal, 2H, H10), 3.34 (broad signal, 2H, H9), 3.04 (s, 3H, H8), 0.21 (s, 9H, SiMe_3), 0.12 (s, 9H, SiMe_3). *Isomer B*: $\delta(\text{ppm}) = 7.53$ (s, 1H, H7), 6.89–6.75 (overlapping signals, 4H, H3 + H4 + H5 + H6), 3.83 (broad signal, 2H, H10), 3.56 (broad signal, 2H, H9), 3.04 (s, 3H, H8), 0.21 (s, 9H, SiMe_3), 0.12 (s, 9H, SiMe_3). $\{^1\text{H}\}^{13}\text{C}$ NMR (101 MHz, CD_2Cl_2 , 298 K): *Isomer A*: $\delta(\text{ppm}) = 154.19$ (C7), 148.58 (C2), 144.60 (C1), 122.92 (C3/C4/C5/C6), 122.45 (C3/C4/C5/C6), 121.80 (C3/C4/C5/C6), 121.25 (C3/C4/C5/C6), 60.75 (C10), 55.63 (C9), 33.45 (C8), 0.67 (SiMe_3), -0.47 (SiMe_3). *Isomer B*: $\delta(\text{ppm}) = 154.19$ (C7), 148.58 (C2), 144.60 (C1), 122.92 (C3/C4/C5/C6), 122.45 (C3/C4/C5/C6), 121.80 (C3/C4/C5/C6), 121.25 (C3/C4/C5/C6), 60.75 (C10), 49.75 (C9), 40.21 (C8), 0.67 (SiMe_3), -0.47 (SiMe_3). **Elemental analysis:** calcd for $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_2\text{Si}_2$: C, 56.76; H, 8.93; N, 8.27. Found: C, 56.37; H, 9.10; N, 9.01.

Synthesis of L2(TMS)₂

Under argon, 1.2 g (5.47 mmol) of L2H₂ were solubilized in 30 mL of dry CH_2Cl_2 . 4.6 mL (32.82 mmol, 6 equiv) of triethylamine were added and the solution was cooled at 0 °C. TMSCl (3.3 mL, 26.26 mmol, 4.8 equiv) was added dropwise and the mixture was then allowed to reach room temperature and stirred overnight. The volatiles were evaporated under vacuum and the crude product was extracted with 20 mL then 2×10 mL of dry diethyl ether *via* a filtrating cannula. The filtrate was evaporated under vacuum affording 1.66 g of L2(TMS)₂ as an orange oil (83% yield). ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 7.81$ (s, 1H, H7), 6.90–6.76 (overlapping m, 4H, H3 + H4 + H5 + H6), 3.79 (broad signal, 1H, H9), 3.70–3.36 (overlapping signals, 4H, H8/H10/H11/H12), 2.09–1.74 (overlapping signals, 4H, H8/H10/H11/H12), 0.21 (s, 9H, SiMe_3), 0.11 (s, 9H, SiMe_3). $\{^1\text{H}\}^{13}\text{C}$ NMR (101 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 151.53$ (C7), 148.57 (C2), 144.91 (C1), 122.84 (C3/C4/C5/C6), 122.45 (C3/C4/C5/C6), 121.77 (C3/C4/C5/C6), 121.26 (C3/C4/C5/C6), 65.90 (C8/C10/C11/C12), 61.12 (C9), 46.49 (C8/C10/C11/C12), 28.21 (C8/C10/C11/C12), 23.60 (C8/C10/C11/C12), 0.69 (SiMe_3), -0.46 (SiMe_3). **Elemental analysis:** calcd for $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_2\text{Si}_2$: C, 59.29; H, 8.85; N, 7.68. Found: C, 58.66; H, 8.51; N, 7.66.

Synthesis of L3(TMS)₂

Under argon, 0.94 g (2.11 mmol) of L3H(TMS) were solubilized in 15 mL of dry CH_2Cl_2 . 0.9 mL (6.3 mmol, 3 equiv) of triethylamine and 0.6 mL (5.1 mmol, 2.4 equiv) of TMSCl were successively added dropwise and the mixture was stirred overnight. The volatiles were evaporated under vacuum and the product was extracted with 3×10 mL of dry diethyl ether *via* a filtrating cannula. The filtrate was evaporated under vacuum and then taken back in 15 mL of pentane. Then volatiles were evaporated affording 927 mg of L3(TMS)₂ as a sticky white solid (85% yield). ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 7.80$ (s, 1H, H7), 7.50–7.42 (overlapping signals, 4H, Ar), 7.42–7.29 (overlapping signals, 6H, Ar), 6.87–6.80 (overlapping signals, 2H, H4 + H5), 6.78 (m, 1H, H3/H6), 6.65 (m, 1H, H3/H6), 4.77 (d, $J = 8.1$ Hz, 1H, H9), 3.51 (m, 1H, H8), 2.62 (m, 1H, H8), 2.19 (m, 1H, H11), 1.98 (m, 1H, H11), 1.52 (m, 1H, H10), 0.86 (m, 1H, H10), 0.22 (s, 9H, SiMe_3), -0.22 (s, 9H, SiMe_3). $\{^1\text{H}\}^{13}\text{C}$ NMR (101 MHz, CD_2Cl_2 , 298 K): $\delta(\text{ppm}) = 152.98$ (C7), 148.81 (C2), 144.84 (C1), 143.02 (Ar), 142.79 (Ar), 130.03 (Ar), 129.93 (Ar), 128.32 (Ar), 128.24 (Ar), 127.96 (Ar), 127.82 (Ar), 122.85 (C4/C5), 122.31 (C4/C5), 121.25 (C3/C6), 121.21 (C3/C6), 84.40 (C12), 68.57 (C9), 47.31 (C8), 28.25 (C11), 22.84 (C10), 1.93 (SiMe_3), 0.81 (SiMe_3). **Elemental analysis:** calcd for $\text{C}_{30}\text{H}_{40}\text{N}_2\text{O}_2\text{Si}_2$: C, 69.72; H, 7.80; N, 5.42. Found: C, 69.78; H, 8.23; N, 5.48.

Synthesis of 1 a

In glovebox, a solution of 124.7 mg (0.64 mmol) of proligand L1H₂ in 4 mL of dried and cold THF was added dropwise to a solution of 181.9 mg (0.64 mmol, 1 equiv) of titanium isopropoxide in cold THF (4 mL). The solution was stirred for 30 min at r.t. and the volatiles were evaporated under vacuum. The product was then washed with 4 mL of pentane before being dried under vacuum affording 169 mg of complex 1 a as a yellow powder (74% yield). ^1H NMR (500 MHz, TDF, 298 K): $\delta(\text{ppm}) = 7.75$ (s, 1H, H7), 6.77 (overlapping signals, 2H, H4 + H6), 6.51 (t, $J = 7.5$ Hz, 1H, H5), 6.43 (d, $J = 7.9$ Hz, 1H, H3), 5.18 (overlapping broad signals, 2H, H9 + $\text{OCH}(\text{CH}_3)_2$), 5.00 (broad signal, 1H, $\text{OCH}(\text{CH}_3)_2$), 4.30 (broad signal ($\Delta\nu_{1/2} = 36.9$ Hz), 1H, H10), 4.12 (broad signal ($\Delta\nu_{1/2} = 29.3$ Hz), 1H, H10), 2.58 (broad signal ($\Delta\nu_{1/2} = 39.0$ Hz), 1H, H9), 2.23 (broad signal ($\Delta\nu_{1/2} = 19.0$ Hz), 3H, H8), 1.40 (broad signal, 3H, $\text{OCH}(\text{CH}_3)_2$), 1.32 (broad signal, 3H, $\text{OCH}(\text{CH}_3)_2$), 1.12 (broad signal, 3H, $\text{OCH}(\text{CH}_3)_2$), 1.07 (broad signal, 3H, $\text{OCH}(\text{CH}_3)_2$). $\{^1\text{H}\}^{13}\text{C}$ NMR (150 MHz, TDF, 298 K): $\delta(\text{ppm}) =$

161.64 (C2), 155.64 (C7), 141.54 (C1), 123.98 (C4/C6), 117.98 (C5), 114.76 (C3), 114.41 (C4/C6), 79.18 (OCH(CH₃)₂), 77.80 (OCH(CH₃)₂), 66.88 (deducted from HSQC, C10), 53.80 (C9), 39.42 (C8), 26.10 (OCH(CH₃)₂). **Elemental Analysis:** calcd for (C₁₆H₂₆N₂O₄Ti)₁₀₀(C₅H₁₂)₂₄: C, 55.01; H, 7.46; N, 7.75. Found: C, 55.45; H, 7.29; N, 7.65.

Synthesis of 2a

In glovebox, a solution of 98.1 mg (0.45 mmol) of proligand L2H₂ in 3 mL of dried and cold THF was added dropwise to a solution of 127.9 mg (0.45 mmol, 1 equiv) of titanium isopropoxide in cold THF (2.5 mL). The solution was stirred for 30 min at r.t. and the volatiles were then evaporated under vacuum. The product was then taken back in 4 mL of pentane before being dried under vacuum affording 130 mg of complex 2a as a yellow powder (75% yield). **¹H NMR (500 MHz, TDF, 298 K):** δ(ppm) = 7.96 (s, 1H, H7), 6.85 (d, J = 7.8 Hz, 1H, H6), 6.74 (t, J = 7.5 Hz, 1H, H4), 6.53 (t, J = 7.6 Hz, 1H, H5), 6.43 (d, J = 7.9 Hz, 1H, H3), 5.21 (broad signal, 1H, H9), 5.15 (m, 1H, OCH(CH₃)₂), 4.97 (m, 1H, OCH(CH₃)₂), 4.11 (m, 1H, H12), 3.93 (m, 1H, H12), 3.07 (m, 1H, H8), 2.16 (broad signal (Δ_{v/2} = 26.3 Hz), 1H, H8), 1.70 (m, 1H, H11), 1.47 (m, 2H, H10), 1.38 (overlapping signals, 4H, H11 + OCH(CH₃)₂), 1.32 (d, J = 6.1 Hz, 3H, OCH(CH₃)₂), 1.11 (d, J = 6.1 Hz, 3H, OCH(CH₃)₂), 1.06 (d, J = 6.3 Hz, 3H, OCH(CH₃)₂). **¹H¹³C NMR (150 MHz, TDF, 298 K):** δ(ppm) = 161.68 (C2), 153.06 (C7), 141.32 (C1), 123.82 (C4), 117.83 (C5), 114.97 (C3), 113.44 (C6), 79.00 (OCH(CH₃)₂), 77.52 (OCH(CH₃)₂), 72.73 (C12), 61.46 (C9), 50.86 (C8), 27.22 (C11), 26.39 (OCH(CH₃)₂), 26.18 (OCH(CH₃)₂), 26.09 (OCH(CH₃)₂), 25.97 (OCH(CH₃)₂), 24.37 (C10). **Elemental Analysis:** calcd for C₁₈H₂₈N₂O₄Ti: C, 56.26; H, 7.34; N, 7.29. Found: C, 56.18; H, 6.87; N, 7.29.

Synthesis of 3a

In glovebox, a solution of 238 mg (0.64 mmol) of proligand L3H₂ in 3.5 mL of dried THF was added dropwise to a solution of 181.9 mg (0.64 mmol, 1 equiv) of titanium isopropoxide in THF (3.5 mL). The solution was stirred for 30 min at r.t. and the volatiles were evaporated under vacuum. The product was then taken back in 5 mL of pentane before being dried under vacuum affording 304 mg of complex 3a as a yellow powder (89% yield). **¹H NMR (500 MHz, TDF, 298 K):** δ(ppm) = 8.23 (s, 1H, H7), 7.55–7.50 (overlapping signals, 2H, Ar), 7.45–7.38 (overlapping signals, 2H, Ar), 7.33–7.26 (overlapping signals, 2H, Ar), 7.26–7.18 (overlapping signals, 4H, Ar), 6.86 (dd, J = 7.9, 1.4 Hz, 1H, H6), 6.80 (td, J = 7.6, 1.5 Hz, 1H, H4), 6.49 (td, J = 7.6, 1.4 Hz, 1H, H5), 6.44 (dd, J = 7.9, 1.4 Hz, 1H, H3), 5.35 (dd, J = 9.0, 4.0 Hz, 1H, H9), 4.64 (m, 1H, OCH(CH₃)₂), 4.39 (m, 1H, OCH(CH₃)₂), 3.52 (m, 1H, H8), 2.64 (m, 1H, H8), 2.45 (m, 1H, H11), 2.20 (m, 1H, H11), 1.60 (m, 1H, H10), 1.06 (d, J = 6.1 Hz, 3H, OCH(CH₃)₂), 0.99 (d, J = 6.0 Hz, 3H, OCH(CH₃)₂), 0.92 (overlapping signals, 4H, OCH(CH₃)₂ + H10), 0.88 (d, J = 6.0 Hz, 3H, OCH(CH₃)₂). **¹H¹³C NMR (150 MHz, TDF, 298 K):** δ(ppm) = 161.94 (C2), 155.36 (C7), 148.15 (Ar), 146.40 (Ar), 141.14 (C1), 129.63 (Ar), 129.26 (Ar), 128.03 (Ar), 127.51 (Ar), 127.34 (Ar), 127.32 (Ar), 125.14 (C4), 117.08 (C5), 114.62 (C6), 114.37 (C3), 89.29 (C12), 78.53 (OCH(CH₃)₂), 76.91 (OCH(CH₃)₂), 69.70 (C9), 53.15 (C8), 29.71 (C11), 26.19 (OCH(CH₃)₂), 26.03 (OCH(CH₃)₂), 25.91 (OCH(CH₃)₂), 25.87 (OCH(CH₃)₂), 22.88 (C10). **Elemental Analysis:** calcd for (C₃₀H₃₆N₂O₄Ti)₁₀₀(C₂H₆O)₄₀: C, 65.34; H, 6.84; N, 4.95. Found: C, 65.26; H, 6.22; N, 4.68 (product contaminated by silicone grease).

Synthesis of 1b

Under argon, a solution of 700 mg (2.07 mmol) of proligand L1(TMS)₂ in 25 mL of dry THF was cannulated at 0 °C on a solution of 691 mg (2.07 mmol, 1 equiv) of TiCl₄(thf)₂ in 25 mL of dry THF.

The mixture was stirred at r.t. for 3 h then heated at 65 °C overnight. The mixture was then cooled and a precipitate was formed. The solid was filtrated in glovebox affording 769 mg of complex 1b (97% yield). **¹H NMR (500 MHz, CD₂Cl₂/TDF, 298 K):** δ(ppm) = 7.93 (s, 1H, H7), 6.92 (m, 1H, H4/H5), 6.68 (overlapping signal, 2H, H3/H6 + H4/H5), 6.46 (d, J = 7.6 Hz, 1H, H3/H6), 4.35 (m, 2H, H10), 3.93 (m, 2H, H9), 3.69–3.53 (4H, THF and TDF overlapping), 3.37 (s (Δ_{v/2} = 1.7 Hz), 3H, H8), 1.82–1.66 (4H, THF and TDF overlapping). **¹H¹³C NMR (150 MHz, CD₂Cl₂/TDF, 298 K):** δ(ppm) = 158.50 (C2), 157.58 (C7), 142.54 (C1), 125.62 (C4), 120.64 (C5), 115.67 (C6), 112.93 (C3), 70.92 (C10), 68.09 (THF), 56.52 (C9), 41.55 (C8), 26.01 (THF). **Elemental Analysis:** calcd for C₁₄H₂₀Cl₂N₂O₃Ti: C, 43.89; H, 5.26; N, 7.31. Found: C, 43.36; H, 5.66; N, 6.92.

Synthesis of 2b

In glovebox, a solution of 1.0 g (2.74 mmol) of proligand L2(TMS)₂ in 25 mL of dry THF was added dropwise to a solution of 915 mg (2.74 mmol, 1 equiv) of TiCl₄(thf)₂ in 25 mL of dry THF at 0 °C. The mixture was allowed to reach r.t. and stirred for 3 h then heated at 65 °C overnight. The mixture was cooled and a precipitate was formed. The solid was filtrated in glovebox affording 970 mg of complex 2b (87% yield). **¹H NMR (500 MHz, CD₂Cl₂/TDF, 298 K):** δ(ppm) = 8.11 (s, 1H, H7), 6.95 (td, J = 7.6, 1.6 Hz, 1H, H4), 6.77 (dd, J = 8.0, 1.6 Hz, 1H, H6), 6.72 (td, J = 7.5, 1.4 Hz, 1H, H5), 6.50 (dd, J = 7.9, 1.5 Hz, 1H, H3), 4.52 (m, 1H, H9), 4.34 (dd, J = 11.9, 3.2 Hz, 1H, H12), 4.07 (m, 1H, H12), 3.90 (m, 1H, H8), 3.82 (m, 1H, H8), 3.69–3.60 (4H, THF and TDF overlapping), 2.24 (m, 1H, H11), 1.99 (overlapping signals, 2H, H10), 1.84–1.73 (4H, THF and TDF overlapping), 1.69 (m, 1H, H11). **¹H¹³C NMR (150 MHz, CD₂Cl₂/TDF, 298 K):** δ(ppm) = 158.34 (C2), 154.48 (C7), 142.43 (C1), 125.76 (C4), 120.60 (C6), 115.00 (C5), 113.24 (C3), 77.10 (C12), 68.16 (THF), 64.10 (C9), 53.49 (deducted from HSQC, C8), 28.07 (C11), 26.01 (THF), 23.96 (C10). **Elemental Analysis:** calcd for C₁₆H₂₂Cl₂N₂O₃Ti: C, 46.97; H, 5.42; N, 6.85. Found: C, 47.18; H, 5.38; N, 7.25.

Synthesis of 3b'

In glovebox, a solution of 517 mg (1 mmol) of proligand L3(TMS)₂ in 5 mL of dried and cold CH₂Cl₂ was added dropwise to a solution of 334 mg (1 mmol, 1 equiv) of TiCl₄(thf)₂ in CH₂Cl₂ (5 mL). The solution was stirred for 50 min at r.t. and the volatiles were evaporated under vacuum to give 669 mg of complex 3b' as a dark red solid (100% yield). **¹H NMR (500 MHz, CD₂Cl₂/TDF, 298 K):** δ(ppm) = 8.55 (s, 1H, H7), 7.48–7.26 (overlapping signals, 10H, Ar), 6.84 (td, J = 7.7, 1.5 Hz, 1H, H4), 6.74 (td, J = 7.6, 1.5 Hz, 1H, H5), 6.33 (dd, J = 8.0, 1.4 Hz, 1H, H3), 6.23 (dd, J = 7.9, 1.5 Hz, 1H, H6), 5.05 (m, 1H, H9), 3.69–3.55 (4H, THF and TDF overlapping), 2.88 (m, 1H, H8), 2.45 (m, 1H, H11), 2.28 (m, 1H, H8), 2.08 (m, 1H, H11), 1.82–1.72 (4H, THF and TDF overlapping), 1.67 (overlapping signals, 2H, H10), –0.11 (s, 9H, SiMe₃). **¹H¹³C NMR (150 MHz, CD₂Cl₂/TDF, 298 K):** δ(ppm) = 158.73 (C7), 157.62 (C2), 143.02 (Ar), 142.33 (C1), 141.93 (Ar), 129.58 (Ar), 129.44 (Ar), 128.91 (Ar), 128.87 (Ar), 128.70 (Ar), 128.41 (Ar), 124.46 (C4), 122.87 (C5), 119.07 (C6), 111.85 (C3), 84.67 (C12), 74.59 (C9), 52.77 (C8), 27.13 (C11), 25.81 (C10), 1.93 (SiMe₃). **Elemental Analysis:** calcd for (C₃₁H₃₉Cl₃N₂O₃SiTi)₁₀₀(CH₂Cl₂)₄₀: C, 53.58; H, 5.70; N, 3.98. Found: C, 53.64; H, 5.92; N, 3.77.

Synthesis of 3b

In glovebox, 480 mg (0.89 mmol) of complex 3a were solubilized into 20 mL of dry THF. 0.45 mL (3.56 mmol, 4 equiv) of TMSCl were then added and the mixture was stirred at r.t. overnight. A dark purple precipitate was formed and filtrated in glovebox to give 498 mg of complex 3b (100% yield). **¹H NMR (500 MHz, CD₂Cl₂/**

TDF, 298 K): δ (ppm)=8.23 (s, 1H, H7), 7.64 (broad signal, 2H, Ar), 7.52–7.26 (overlapping signals, 8H, Ar), 6.99 (t, $J=7.6$ Hz, 1H, H4), 6.79 (d, $J=7.7$ Hz, 1H, H6), 6.76 (t, $J=7.5$ Hz, 1H, H5), 6.49 (d, $J=7.6$ Hz, 1H, H3), 5.51 (broad signal, 1H, H9), 3.82–3.54 (overlapping signals, H8+THF+TDF), 2.84 (broad signal, 1H, H8), 2.53 (m, 1H, H11), 2.25 (m, 1H, H11), 1.96–1.70 (THF and TDF overlapping), 1.68 (m, 1H, H10), 0.96 (broad signal, 1H, H10). **$\{^1\text{H}\}^{13}\text{C}$ NMR (150 MHz, CD_2Cl_2 /TDF, 298 K):** δ (ppm)=158.80 (C2), 156.00 (C7), 143.16 (Ar), 141.87 (C1), 129.77 (Ar), 129.35 (Ar), 128.59 (Ar), 128.47 (Ar), 128.34 (Ar), 128.17 (2xAr), 126.09 (C4), 120.24 (C5), 114.35 (C6), 113.15 (CH, C3), 92.79 (C12), 70.44 (C9), 68.18 (THF), 54.54 (C8), 29.18 (C11), 26.00 (THF), 22.24 (C10). **Elemental Analysis:** calcd for $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{N}_2\text{O}_3\text{Ti}$: C, 59.91; H, 5.39; N, 4.99. Found: C, 59.47; H, 5.64; N, 5.01.

Procedure for the Trimethylsilylcyanation of Aldehydes

In glovebox, 0.025 mmol (0.05 equiv) of catalyst was introduced into a Schlenck and solubilized into 1 mL of dry CH_2Cl_2 . 0.5 mmol of aldehyde were then added with a microsyringe. Out of the glovebox, the mixture was put in a bath at a given temperature and TMSCN (1 mmol, 2 equiv) was added dropwise with a microsyringe. Several samples were made at different times by taking about 25 μL of mixture and solubilizing it into CDCl_3 . The conversion was then determined by NMR integration of the silylether derivative (compared to RCHO). After completion, the solution was hydrolyzed with a mixture of 4 mL of HCl_{aq} 1 M and 10 mL of AcOEt. The phases were separated and the product extracted twice with 15 mL of AcOEt. The organic phases were combined, dried over MgSO_4 and evaporated under vacuum.

Conversion to the Corresponding Acetate

The residue was taken back into 2.5 mL of CH_2Cl_2 and 162 μL of pyridine and 96 μL of Ac_2O were successively added. After 1 h30 (or overnight), the mixture was hydrolyzed with 10 mL of HCl_{aq} 1 M. The product was then extracted three times with 20 mL of AcOEt. The organic phases were combined, dried over MgSO_4 and evaporated under vacuum.

2-O-Acetyl-2-phenyl acetonitrile: ^1H NMR (400 MHz, CDCl_3 , 298 K): δ (ppm)=7.56–7.49 (overlapping signals, 2H, Ar), 7.48–7.43 (overlapping signals, 3H, Ar), 6.42 (s, 1H, CH), 2.17 (s, 3H, CH_3). Retention time (GC): $t_1=15.25$ min (R), $t_2=15.40$ min (S). $[\alpha]_D^{20}=+4.3$ ($c=0.77$) for 74% ee (R) (litt.^[26]: $[\alpha]_D^{20}=+7.8$, $c=5$ for (R) enantiomer).

2-O-Acetyl-3,3-dimethylbutyronitrile: ^1H NMR (400 MHz, CDCl_3 , 298 K): δ (ppm)=5.07 (s, 1H, CH), 2.16 (s, 3H, CH_3), 1.10 (s, 9H, tBu). Retention time (GC): $t_1=8.87$ min (R), $t_2=9.24$ min (S). $[\alpha]_D^{20}=+69$ ($c=0.62$) for 60% ee (R) (litt.^[27]: $[\alpha]_D^{20}=+108.7$, $c=1.1$ for (R) enantiomer, 91%).

Computational Details

All Quantum mechanics calculations were performed using the Gaussian 16 package.^[28] Energy and forces were computed by density functional theory with the hybrid B3PW91 exchange-correlation functional,^[29] in THF described by the PCM approach. Geometries were optimized and characterized with the def2-SVP basis set.^[30] Gibbs free energies have been computed at 298 K and 1 atm using unscaled density functional frequencies at the same level.

Supporting Information Summary

The authors have cited additional references within the Supporting Information.^[31–37]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

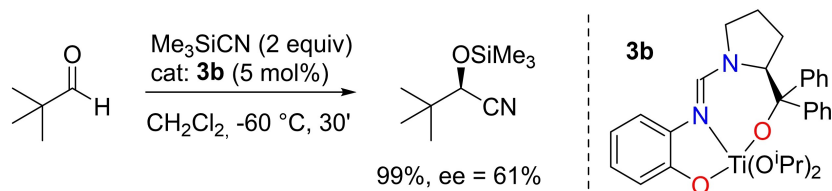
Keywords: Silylcyanation · Amidine · Titanium · Prolinol

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RESEARCH ARTICLE



Here we report the synthesis of new chiral tridentate phenoxy-amidine ligands derived from prolinol and their Ti-complexes. Complex **3b** was found to be highly active for the silylcyanation of pivaldehyde, yielding the

cyanohydrin derivative with 61% ee, a value close to that reported previously by Oguni with a valinol-derived tridentate Schiff base titanium complexes.

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Prolinol-Derived Phenoxy-Amidine Titanium Complexes in Asymmetric Silylcyanation of Aldehydes

