Synthesis of Titanium and Vanadium Diamine Bis(Phenolate) Complexes. Application of Ti Catalysts to the Pinacol Coupling Reaction

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Diamine bis(phenolate) ligand precursors 6,6'-(2-(dimethylamino)ethylazanediyl) bis(methylene)bis(2,4-di-tert-butylphenol) (**H₂L¹**, **1**) and (*S*)-6,6'-((1-ethylpyrrolidin-2-yl) methylazanediyl) bis(methylene)-bis(2,4-di-tert-butylphenol) (**H₂L²**, **2**) were used to prepare titanium and vanadium complexes. The compounds, with formulas [VOL²(OⁱPr)] (**3**), [TiL¹Cl(THF)] (**4**), [TiL¹Cl]₂(μ-O) (**5**), [TiL¹(OⁱPr)₂] (**6**) and [TiL¹Cl₂] (**7**) were characterized by NMR and elemental analysis, and the molecular structures of **3** and **7** were obtained by single crystal X-ray diffraction.

The reactivity of the titanium complexes [TiL¹Cl₂] and [TiL¹Cl]₂(μ-O) towards the pinacol coupling of benzaldehyde was tested and optimized in relation to the following parameters: i) catalyst precursor ii) metallic reductant (Mg, Sn, Zn, Mn), iii) catalyst to benzaldehyde proportion (from 1% to 20%), iv) reaction temperature (between 0ºC and 55ºC) and v) solvent (THF and toluene). It was found that the best results were obtained using [TiL¹Cl₂] and Mn/TMSCl in THF at 55ºC. This system gave complete conversion of benzaldehyde to its pinacol product PhCH(OH)CH(OH)Ph with a diastereomeric excess of 71%, when the ratio [Ti]:benzaldehyde is 15%, and of 67 % when it is 7,5%.

Keywords: Titanium, Vanadium, Diamine Bis(Phenolates), Pinacol Coupling, Catalysis

Introduction

Low-valent titanium species have a long and prolific history in electron-transfer reactions, both in catalytic and stoichiometric processes. Titanium species have been employed to promote the reductive ring opening of epoxides to alkenes and alcohols, the reduction of alkyl and aryl halides, the reductive deoxygenation of alcohols, the opening of strained rings and the reductive coupling of carbonyl compounds to alkenes and dialcohols.[1–11]

The most powerful tools in titanium catalyzed C-C bond formation are undoubtedly the McMurry and the pinacol coupling reactions, in which two carbonyl groups from ketone or aldehyde molecules are coupled to give an alkene or diol, respectively (Figure 1). The catalysts are low-valent titanium species usually obtained *in situ* using a reducing agent.
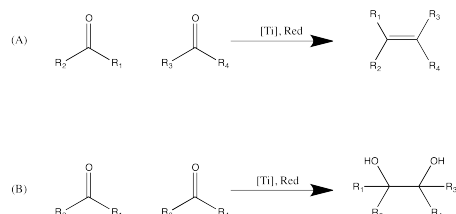

Figure 1: The McMurry (A) and Pinacol Coupling (B) reactions

Recently, new catalytic versions of the pinacol coupling reaction have been developed. Dunlap and Nicholas showed that using Cp₂TiCl₂ as the catalyst precursor and either Mn or Mg as reducing agents, it is possible to obtain pinacol products in good yield and diastereomer selectivity.[12,13]

Reactions of stoichiometric amounts of Cp₂TiCl with the benzaldehyde confirmed that the oxidation state is Ti(III). Furthermore, the stereoselectivity of the reaction depends on the form of the titanocene chloride present in solution: the monomeric form of the catalyst gives preferably the meso-product while the dimeric form gives the dl- product (Figure 2).[13]
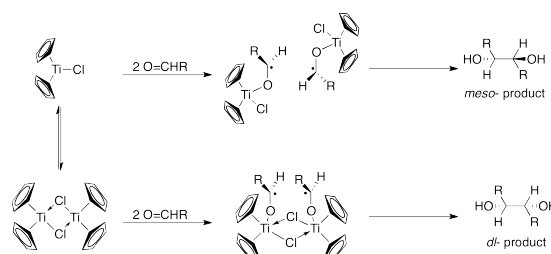

Figure 2: Different products obtained from the monomeric and dimeric forms of the Cp₂TiCl catalyst, with the steric effects shown.

Other organometallic complexes of titanium, displaying chiral ligands, have also been applied in the pinacol coupling reaction with the purpose of obtaining enantiopure products. Very few studies have so far been published and only a few types of ligands have been tested, some of which are shown in Figure 3.[8,14–18] Titanium complexes of the SALEN ligand (a) and other chiral Schiff bases such as (b) were tested in both stoichiometric and catalytic conditions and the most active co-catalyst system was found to be the Mn/TMSCl mixture at 0ºC. Complexes of tartaric acid derivatives, such as TADDOL (c) and chiral ethers (d) have also been found to give good results using Zn/TMSCl, both with aromatic and aliphatic aldehydes.[17–19]
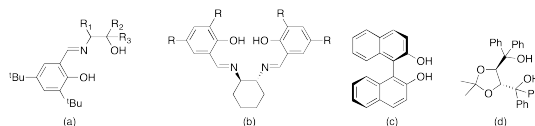

Figure 3: Examples of chiral ligands used in enantioselective pinacol coupling reactions.

Anionic polydentate ligands containing oxygen and/or nitrogen donors have proven particularly well suited for early-transition metals, which are highly acidic and oxophylic. The hard nature of the N and O donors gives thermodynamic stability to the complexes and the ligand topologies provide kinetic stabilization, well-defined coordination geometries and strong steric protection of the metallic centers.[20–24]

Diamine bis(phenolate) ligands have long been used in coordination chemistry with late transition metals[25–27] and more recently in complexes of early transition metals of Group 3 (Sc, Y), Group 4 (Ti, Zr, Hf) and Group 5 (V, Ta).[28–30] Several of these complexes have been applied in catalysis,

particularly olefin and cyclic esters polymerizations,[31–34] epoxidations,[35,36] and sulfoxidations.[37–39]

Martins and co-workers reported in recent years the synthesis, reactivity and catalytic aplications of several new diamine bis(phenolate) complexes of Ti, Zr, V, Mo and W, using both achiral (**A**) and chiral (**B** and **C**) ligand precursors (Figure 4).[39–43]
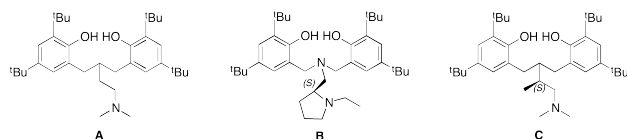

Figure 4: Ligand precursors used by Martins *et al*. for diamine bis(phenolate) complexes of Group 4, 5 and 6 metals

In this work, we attempt the establishment of new synthetic methods for titanium and vanadium complexes of diamine bis(phenolate) ligands A and B. We also report the assessment of the titanium complexes reactivity towards the pinacol coupling reaction.

Results and Discussion

The ligand precursors used in this work, 6,6'-(2-(dimethylamino)ethylazanediyl) bis(methylene)bis(2,4-di-tert-butylphenol) (**H$_2$L^1**, **1**) and (*S*)-6,6'-((1-ethylpyrrolidin-2-yl)methylazanediyl)bis(methylene)- bis(2,4-di-tert-butylphenol) (**H$_2$L^2**, **2**), were synthetized through a single-step Mannich condensation reaction following the procedures reported in the literature.[44]

[VO(L^2)O^{i}Pr] (**3**), was obtained as a dark brownish solid in 60% yield from the reaction of [VO(O^{i}Pr)$_3$] with **H$_2$L^2**.

As is to be expected for a rigid asymmetric complex, the NMR shows distinct resonances for all protons. The spectrum also shows a set of peaks of much lower intensity at slightly different chemical shifts and with the same multiplicity, which indicate the presence of a minor isomer. Four isomers of complex **3**, shown in Figure 5, are possible. The molecules labelled **a** and **b** display *trans*-phenolate moieties whereas the other two isomers, **c** and **d**, show *cis*-phenolate bonding. The latter structures are usually less stable than the former, leading to the assumption that the two isomers that are seen in the ^{1}H NMR spectrum correspond to structures **a** and **b**.[39]
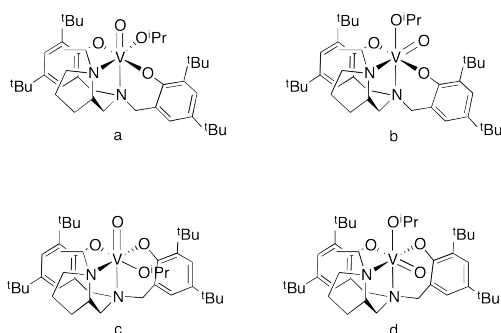

Figure 5: Possible isomers of 3.

Brownish crystals of **3** suitable for X-ray diffraction were grown from a toluene/hexane solution. The compound crystallizes in the monoclinic system, space group *P*2$_1$, with four molecules in the asymmetric unit. The four molecules differ mainly in the coordination mode of the diamine side arm. An ORTEP view of one of the molecules, **3a**, is depicted in Figure 6 and selected structural parameters for **3a-3c** are listed in Table 1.
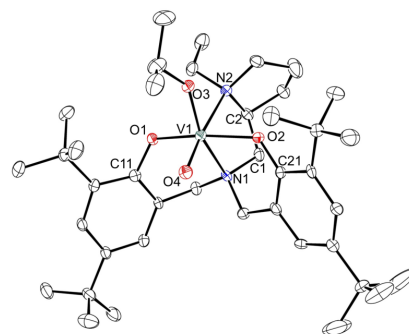

Figure 6: ORTEP-3 diagram of [VOL^2(O^{i}Pr)] (3a), using 40 % probability level ellipsoids. Hydrogen atoms are omitted for clarity.

Compound **3** presents distorted octahedral geometry with the equatorial plane defined by atoms O1, O2 and N2 of L2 and the oxo ligand ligand (O4), while the axial positions are occupied by the isopropoxido ligand (O3) and the tripodal nitrogen N1. The crystallized isomer presents the oxo ligand *cis* to the tripodal nitrogen, as was also observed for the analogous alkoxido diamine bis(phenolate) vanadium complex [VO(L^1)O^{i}Pr], synthetized and characterized in previous studies.[39] The ethylpyrrolidine moiety is coordinated to the metal through the nitrogen atom N2. Chiral atoms N2 and C2 have *S* configuration in the four molecules. The V=O and V-O$_{phenolate}$ bond distances are in the expected ranges for such bonds.[45–47] The phenolate moieties adopt *trans* configuration bending towards the oxo ligand and define dihedral angles of 109.71(1)° to 121.72(1)° between the aromatic planes.

Table 1: Selected structural parameters for 3a-3d.

Distances (Å)				
	a	b	c	d
V(1)-N(1)	2.249(3)	2.234(3)	2.231(3)	2.231(3)
V(1)-N(2)	2.460(3)	2.495(3)	2.426(4)	2.472(3)
V(1)-O(1)	1.912(2)	1.902(2)	1.898(2)	1.910(2)
V(1)-O(2)	1.899(2)	1.890(2)	1.909(2)	1.910(2)
V(1)-O(3)	1.774(3)	1.770(3)	1.772(2)	1.761(2)
V(1)-O(4)	1.590(3)	1.596(3)	1.595(3)	1.595(3)
V(1)-eq. plane^a	0.209(1)	0.222(1)	0.216(1)	0.224(1)
Angles (º)				
O(1)-V(1)-O(2)	161.00(11)	160.21(12)	160.30(12)	160.24(12)
O(1)-V(1)-O(3)	96.16(11)	97.40(11)	97.16(11)	98.20(11)
O(2)-V(1)-O(3)	97.46(11)	94.60(11)	95.29(11)	94.34(11)
O(1)-V(1)-N(1)	83.48(10)	83.51(11)	83.35(11)	83.44(11)
O(2)-V(1)-N(1)	78.65(10)	79.61(11)	79.44(11)	79.37(10)
O(3)-V(1)-N(1)	155.65(12)	158.54(13)	158.19(13)	158.64(12)
O(1)-V(1)-N(2)	83.27(10)	80.13(10)	83.69(11)	80.87(10)
O(2)-V(1)-N(2)	85.75(10)	85.35(11)	82.74(11)	85.22(11)
O(3)-V(1)-N(2)	81.32(11)	84.89(12)	83.00(12)	84.44(11)
N(1)-V(1)-N(2)	74.37(10)	74.11(11)	75.36(11)	74.76(11)
O(1)-V(1)-O(4)	95.04(11)	95.92(12)	95.76(13)	95.47(12)
O(2)-V(1)-O(4)	93.43(12)	95.49(12)	94.93(12)	95.31(13)
O(3)-V(1)-O(4)	107.52(13)	107.17(14)	107.66(13)	107.29(13)
N(1)-V(1)-O(4)	96.79(12)	94.00(13)	93.93(13)	93.68(13)
N(2)-V(1)-O(4)	171.16(12)	167.76(12)	169.28(12)	168.15(12)
θ^b	109.71(1)	122.63(1)	123.24(1)	121.72(1)

^{a} The equatorial plane is defined by atoms O1, O2, N2 and O4.
^{b} θ is the dihedral angle between the planes containing the phenolate rings.

The paramagnetic complex [Ti^{III}L^{1}Cl(THF)] (**4**) was obtained by adding **Na$_2$L^1** (prepared in situ by reacting **H$_2$L^1** with two equivalents of NaH) to a THF solution of the bright blue TiCl$_3$(THF)$_3$, following a procedure previously developed in the group and shown in Figure 7.[40,48] The reaction mixture quickly turned to a yellowish orange that gave an orange-yellow powder in 38% yield after workup.
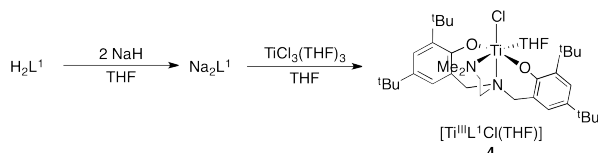
Figure 7: Synthesis and structure of complex 4.

Complex **4** is extremely sensitive to air and moisture, oxidizing to [Ti^{IV}L^{1}Cl]$_2$(μ-O) (**5**) (Figure 8) that was obtained as a dark red solid in 85% yield.
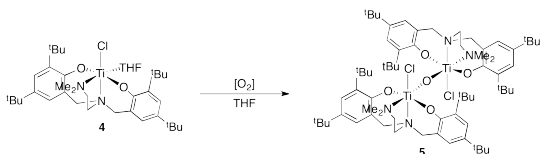

Figure 8: Oxidation of 4 by air to give the oxo-bridged dimer 5

Complex **5** may be converted to the monomeric [TiL^1(O^{i}Pr)$_2$] (**6**) by reaction with isopropanol, in the presence of a base such as triethylamine, through the cleavage of the oxygen bridge. Through this method the compound may be obtained as a bright yellow solid in 75% yield. Complex **6** may alternatively be prepared in 96% yield by directly adding a solution of commercial Ti(OiPr)$_4$ to the ligand precursor **H$_2$L^1** in diethyl ether. Both reactions are schematized in Figure 9.
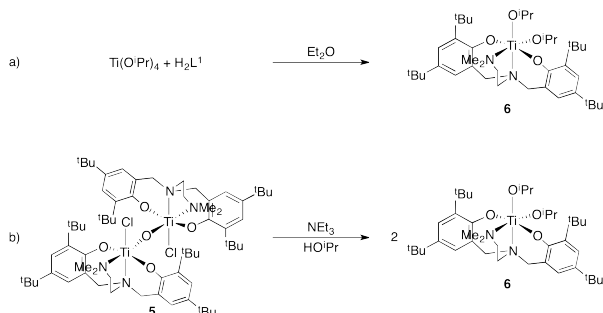

Figure 9: Syntheses of 6 from the dimer 6 (a) and from commercial Ti(OiPr)$_4$ (b)

Compound **6** was reacted with two equivalents of TMSCl in dichloromethane to give [Ti^{IV}L^{1}Cl$_2$] (**7**) in 89% yield. The synthesis of **7** was also attempted from the reaction of [TiCl$_2$(acac)$_2$] with **H$_2$L^1** in THF, but it was unsuccessful, giving a mixture of products. Both reactions are schematized in Figure 10. The NMR data obtained for compound **7** are in agreement with those reported in the literature.[42]
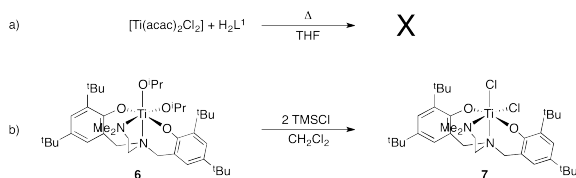

Figure 10: Synthesis of 7 from 6 (a) and reaction of [Ti(acac)$_2$Cl$_2$] with H$_2$L^1 (b)

Orange crystals of 7 suitable for X-ray diffraction were grown from a toluene/hexane double layer solution. The compound crystallizes in the monoclinic system, space group P2$_1$/a, with one molecule in the asymmetric unit. The molecular structure of 7 is depicted in Figure 11 and selected structural parameters are listed in Table 2.
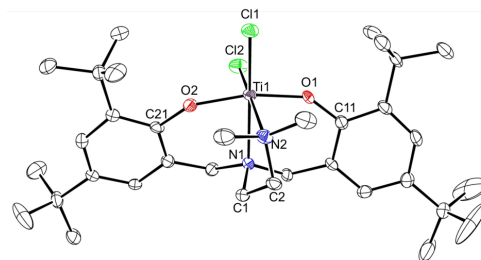

Figure 11: ORTEP-3 diagram of 7, using 40 % probability level ellipsoids. Hydrogen atoms are omitted for clarity.

The titanium coordination geometry is distorted octahedral with the equatorial plane defined by atoms O1, O2 and N2 of **L^1** and the chloride ligand Cl2, while the tripodal nitrogen N1 and the chloride ligand Cl1 occupy the axial positions. The titanium is slightly away from the equatorial plane [0.199(2) Å] towards Cl1. The two phenolate moieties occupy *trans* positions with a dihedral angle of 159.0(2)° between the phenolate ring planes. The sidearm fragment is coordinated to the metal and the tripodal ligand forces the two chloride ligands to adopt mutually *cis* dispositions. The Ti-O and Ti-N distances are within the expected values and compare well with values reported for octahedral titanium(IV) diamine (bis)phenolate complexes,[21,22,24,30,49] and the Ti-Cl distances also fit values reported for titanium(IV) systems supported by O- and N- based ligands.[50–52]

Table 2: Selected structural parameters for 7

Distances (Å)			
Ti(1)-O(1)	1.831(3)	Ti(1)-N(2)	2.307(4)
Ti(1)-O(2)	1.838(3)	Ti(1)-Cl(1)	2.304(1)
Ti(1)-N(1)	2.275(3)	Ti(1)-Cl(2)	2.307(1)
Ti(1)-eq. plane^a	0.191(1)		
Angles (°)			
O(1)-Ti(1)-O(2)	166.5(1)	N(1)-Ti(1)-N(2)	78.0(1)
O(1)-Ti(1)-N(1)	85.2(1)	N(1)-Ti(1)-Cl(1)	165.3(1)
O(1)-Ti(1)-N(2)	86.8(1)	N(1)-Ti(1)-Cl(2)	93.0(1)
O(1)-Ti(1)-Cl(1)	97.6(1)	N(2)-Ti(1)-Cl(1)	88.0(1)
O(1)-Ti(1)-Cl(2)	90.0(1)	N(2)-Ti(1)-Cl(2)	170.6(1)
O(2)-Ti(1)-N(1)	81.4(1)	Cl(1)-Ti(1)-Cl(2)	101.4(1)
O(2)-Ti(1)-N(2)	91.3(1)	Ti(1)-O(1)-C(11)	146.0(3)
O(2)-Ti(1)-Cl(1)	95.6(1)	Ti(1)-O(2)-C(21)	144.0(3)
O(2)-Ti(1)-Cl(2)	89.8(1)	θ^b	176.8(2)

^{a} The equatorial plane is defined by atoms O1, O2 and N2 and Cl2.
^{b} θ is the dihedral angle between the planes containing the phenolate rings.

The procedure used for the pinacol coupling reaction was adapted from the literature.[16] The catalytic study involved optimization of several parameters such as the nature of the catalyst, the catalyst:substrate ratio, the reducing agent, the reaction temperature and the solvent. Benzaldehyde was used in the pinacol coupling reaction to give 1,2-bis(phenyl)-1,2-ethanediol, a well-defined pinacolate with two chiral centers that has two diastereomers, one of which is chiral (Figure 12).
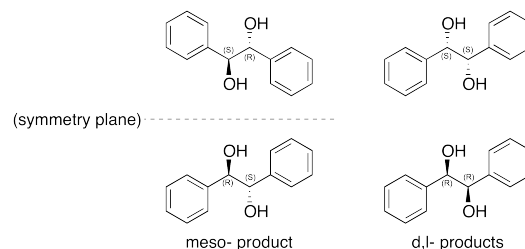

Figure 12: The products of the pinacol coupling of two benzaldehyde molecules: on the left, the *meso-* diastereomer, and on the right the two enantiomers of the *dl-* diastereomer.

Specific peaks in ^{1}H NMR spectra can be used to identify both the reagent (PhC*H*O, 1H, singlet, 10.03 ppm)

and the two diastereomers (PhC*H*OHC*H*OHPh, 2H, singlet, 4,73ppm (*dl*) and 4,83 ppm (*meso*)), as shown in Figure 13. The integration of the ^{1}H NMR spectra using the benzaldehyde proton as reference allowed quantitative information of conversion, diastereomeric proportion and diastereomeric excess, without the need to fully purify the product. Expressions 1-3 were used for the calculations.

$$Conversion\ (\%) = \frac{\frac{\int dl}{2}+\frac{\int meso}{2}}{\frac{\int dl}{2}+\frac{\int meso}{2}+\int benzaldehyde}\times100 \qquad (1)$$

$$Diastereomer\ Excess = \frac{\int dl-\int meso}{\int dl+\int meso}\times100 \qquad (2)$$

$$Diastereomer\ Fraction\ (dl:meso) = \frac{\int dl}{\int meso} \qquad (3)$$

A preliminary test for the pinacol coupling reaction was made using [Ti^{IV}L^{1}Cl]$_2$(µ-O), **5** , magnesium flakes as the metallic reducing species and THF as the solvent. The catalyst was used in 7,5% relative to the benzaldehyde, which corresponds to a ratio of 15% Ti:benzaldehyde. The reaction proceeded for 16 hours at room temperature, under nitrogen leading to 43% conversion and 11% diastereomeric excess.
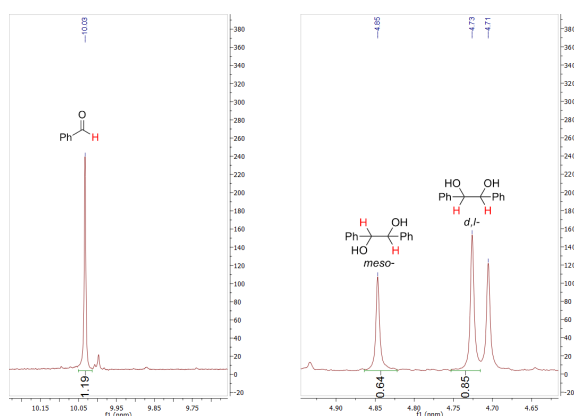

Figure 13: Portions of the ^{1}H NMR spectra of the crude product of reaction A evidencing the peaks that identify the benzaldehyde (s, 10,03 ppm) the *meso*- product (s, 4,85 ppm) and the *dl*- product (s, 4,73 ppm).

Two blank tests were made, one without titanium and the other without Mg/TMSCl. The results, shown in Table 3, clearly confirm that in the absence of either reagent the reaction does not take place.

Table 3: Results of preliminary pinacol coupling tests^a

ID	Catalyst	%	Reductant	Conv.	D. E.
A	[TiL^{1}Cl]$_2$(µ-O)	15%	Mg/TMSCl	43%	14,1%
B	[TiL^{1}Cl]$_2$(µ-O)	15%	Blank Test	1%	73,9%
C1	Blank Test	-	Mg/TMSCl	6%	0,0%

^{a}*The conversion and diastereomeric excess were obtained from the ^{1}H NMR spectra of the product mixture after work-up*

Complex [TiL^{1}Cl$_2$] (**7**) was also tested as catalyst in the same conditions, using 5% of **7.** The mixture changed from dark orange to greenish yellow, which is a typical color indicative of the presence of Ti^{III} species, minutes after the addition of magnesium flakes and TMSCl. After addition of benzaldehyde the mixture returned back to orange. The conversion of benzaldheyde was 15% and the diastereomeric excess is far superior, at 26% (**C1**, Table 4). It was therefore concluded that the [Ti^{IV}L^{1}Cl$_2$] complex is a more active catalyst than dimer the [Ti^{IV}L^{1}Cl]$_2$(µ-O), as expected.

Table 4: Summary of the results obtained with several different metals and the respective blank tests.^{a}

ID	Catalyst	%	Reductant	Conv.	D. E.
C2	[TiL^{1}Cl$_2$]	5%	Mg/TMSCl	15%	26%
D1	Blank Test	-	Mn/TMSCl	11%	58%
D2	[TiL^{1}Cl$_2$]	5%	Mn/TMSCl	82%	34%
E1	Blank Test	-	Zn/TMSCl	86%	-4%
E2	[TiL^{1}Cl$_2$]	5%	Zn/TMSCl	88%	16%
F1	Blank Test	-	Sn/TMSCl	4%	100%
F2	[TiL^{1}Cl$_2$]	5%	Sn/TMSCl	0%	0%

The most efficient reducing species for the activation of Ti^{IV} was assessed by comparison of reactions that used magnesium, zinc, tin and manganese. For each metal, a blank reaction was performed. The results are summarized in Table 4.

Zinc was found to be the most active metal but its role in the reaction is not only as a reducing agent because the reaction takes place even in the absence of the titanium catalyst. Indeed, Zinc is *per se* a catalyst for the pinacol coupling reaction in acidic conditions.[53] It should be noted that Magnesium has also been reported to have similar catalytic activity in the pinacol coupling reaction, but that was not observed in this study.[53,54] Apart from Zinc, none of the metals tested are able to promote the reaction in the absence of the titanium precursor and Tin revealed inappropriate for the reduction of Ti. The best results were obtained with Manganese powder.

The influence of the amount of catalyst was tested within the range of 1% to 20% in relation to the benzaldehyde. In Table 5 it can be seen that the reaction occurs even with 1% catalyst but the activity increases greatly with the amount of catalyst. With 7.5% catalyst, a local maximum is reached (92% conversion, **G3**), making this the most efficient proportion (conversion/catalyst), although higher proportions of catalyst give better conversions in absolute terms. The diastereomeric excess, on the other hand, doesn't have a direct correlation with that ratio, reaching its maximum at 15% of catalyst.

Table 5: Summary of the results obtained with several different catalyst proportions.^{a}

ID	Catalyst	%	TºC	Reductant	Conv.	D. E.
G1	[TiL^{1}Cl$_2$]	1,0%	20ºC	Mn/TMSCl	34%	23,5%
G2	[TiL^{1}Cl$_2$]	2,5%	20ºC	Mn/TMSCl	80%	38%
G3	[TiL^{1}Cl$_2$]	7,5%	20ºC	Mn/TMSCl	92%	37%
G4	[TiL^{1}Cl$_2$]	10%	20ºC	Mn/TMSCl	91%	25%
G5	[TiL^{1}Cl$_2$]	15%	20ºC	Mn/TMSCl	94%	48%
G6	[TiL^{1}Cl$_2$]	20%	20ºC	Mn/TMSCl	98%	28%

The reaction was tested at low-temperature (0ºC) and high-temperature (55ºC) conditions using two catalyst proportions: the most efficient, 7,5% catalyst, and the most stereoselective, 15% (Table 6). Both the conversion and the stereoselectivity greatly increase with temperature: at 55ºC the reaction can be considered complete in both cases (**I1** and **I2**), and the essay using 15% of Ti (**I2**) gave 71% diastereomeric excess (d.e.); on the other hand, at 0ºC only 50% conversion and 31% d.e. was attained in similar conditions (**H2**). This is particularly interesting because it differs from the results found in the literature, according to which the lower temperature greatly increases the stereoselectivity and the yield when using both titanocene- and Schiff ligand-based titanium catalysts.[9,16,19,55] Considering these results, two additional tests were carried out: a blank at 55ºC (**J**), which yielded a modest conversion with inverted diastereoselectivity, and a medium-temperature reaction at 45ºC with 7,5% catalyst (**K**), which gave slightly lower conversion and diastereomeric excess.

Table 6: Summary of the results obtained at several different temperatures and respective blank tests.^{a}

ID	Catalyst	%	TºC	Conv.	D. E.
H1	[TiL^{1}Cl$_2$]	7,5%	0ºC	44,8%	16 %

H2	[TiL^{1}Cl$_2$]	15.0%	0°C	49.7%	31%
I1	[TiL^{1}Cl$_2$]	7.5%	55°C	99.7%	67%
I2	[TiL^{1}Cl$_2$]	15.0%	55°C	99.7%	71%
J	Blank Test	-	55°C	24.0%	-49%
K	[TiL^{1}Cl$_2$]	7,5%	40°C	96.3%	58.5%
L*	[TiL^{1}Cl$_2$]	7,5%	55°C	76.9%	11%

*Solvent: Toluene

A final test was made to check whether the solvent had a significant effect on the reaction. A reaction carried in toluene at 55°C (Table 6, **L**) led to a conversion of 77% and a diastereomeric excess of only 11%. This indicates that the more polar environment of THF is a key factor in the reaction mechanism, increasing not only the yield but also the selectivity. Considering that THF is a coordinating solvent, it may force a specific conformation of a reaction intermediate.

The comparison of complex **7** with other catalysts found in the literature (shown in Error! Reference source not found.) shows that it has a very good activity and may have potential for future applications in the pinacol coupling reaction. The major drawback of the system is the diastereoselectivity, which is slightly lower than for other catalysts, particularly those with chiral ligands. This shows that the achiral **L^1** ligand does not control the reaction center's geometry as much as, for example, chiral Schiff bases.

A mixture of **6** and Zinc powder in THF led to the reduction of Ti(IV) to Ti(III). The EPR spectra of that sample, taken before and immediately after the addition of benzaldehyde, clearly indicate the existence of paramagnetic species before and after the addition of benzaldehyde. The complexity of the spectra reveals the presence of more than one Ti(III) species in both cases, which may correspond to the formation of conformational isomers or to different complexes. Immediately after the addition of benzaldehyde some of the signals disappear.

A stoichiometric reaction between complex [TiL^{1}Cl(THF)] (**5**) and benzaldehyde was carried out in THF at room temperature (NMR tube scale). This reaction was characterized by ^{1}H NMR in CDCl$_3$, revealing the formation of the pinacol product with 72% conversion. This result indicates that [TiL^{1}Cl] is able to catalyze the reaction although it is interesting to note that the stoichiometric reaction gives no diastereomeric excess, unlike the catalytic reactions. This result may indicative that the role of the reducing metal species is not only the reduction of the Ti(IV) to Ti(III), but it influences the reaction selectivity, possibly by forming metallic aggregates of the type [Ti]-Mn-[Ti].

A tentative proposal for the catalytic sequence, based on this result and on literature information, is shown in Figure 14. Previous studies have shown that the THF ligand in [TiL^{1}Cl(THF)] is labile.[42] Its dissociation gives [TiL^{1}Cl], which is likely the active species that coordinates and reduces the aldehyde by electron-transfer from the Ti center to the carbonyl carbon. The coupling of two radicals, which possibly involves two [TiL^1(Cl)(OCHPh)] moieties, eventually displaying chloride or phenolate bridging ligands to Mn, may lead to the release of the product in presence of TMSCl. A Ti(IV) dichloride complex may then be formed. In catalytic conditions, the reduction of Ti(IV) to Ti(III) is achieved through electron transfer from Mn.
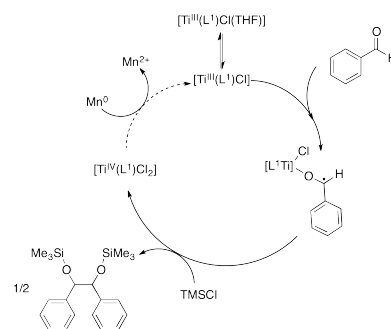

Figure 14: Tentative catalytic sequence for the [TiL^{1}Cl$_2$] catalysed pinacol coupling

Concluding Remarks

The ligand precursors **H$_2$L^1** and **H$_2$L^2** were successfully synthetized. The synthesis of the novel complex [VO(L^2)O^{i}Pr] (**3**) and its molecular structure were achieved. The syntheses of titanium complexes **4** to **7** were also obtained and a new synthetic method for [TiL^1(OiPr)$_2$] (**6**) from commercially available Ti(OiPr)$_4$ was described.

Titanium complexes **5** and **7** were tested as catalysts precursors for the pinacol coupling of benzaldehyde, and several experimental factors were optimized. It was concluded that the best system is [TiL^{1}Cl$_2$] with Mn/TMSCl as reductant in THF at 55°C. Both 7,5% and 15% [Ti]:benzaldehyde proportions gave complete conversion in these conditions and the diastereomeric excesses obtained varied only slightly (67% to 71%, respectively). In the future, it would be interesting to test chiral ligands of the same kind in an effort to obtain better diastereomeric excesses and ultimately enantioselectivity.

EPR and NMR experiments were run in order to get information about the catalytic reactions. The EPR spectra showed the presence of Ti(III) species in the reaction medium, some of which are quenched by addition of benzaldehyde. Furthermore, the stoichiometric reaction of [TiL^{1}Cl(THF)] with benzaldehyde showed no diastereoselectivity, which may indicate that the metal reductant plays a role in the catalysis mechanism in addition to its reducing function. The interaction between Ti and the reducing metals is likely to occur in solution and this interaction is important in determining the diastereomeric excess dl:meso.

Experimental Section

General Considerations

All preparations and subsequent manipulations of air/moisture sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk line and glovebox techniques. THF, toluene, n-hexane, CH$_2$Cl$_2$ and Et$_2$O were dried by standard methods (sodium/benzophenone for THF, toluene and Et$_2$O; calcium hydride for n-hexane and CH$_2$Cl$_2$) and distilled prior to use. Benzaldehyde was washed with a 5% aqueous solution of Na$_2$CO$_3$, dried with CaCl, distilled under vacuum and kept under inert N$_2$ atmosphere.

NMR samples of air/moisture sensitive compounds were prepared in a glovebox under inert atmosphere using NMR tubes equipped with J-Young stopcocks. The C$_6$D$_6$ used for NMR samples was dried over Na and distilled under reduced pressure.

Unless stated otherwise, all reagents were purchased from commercial suppliers (e. g. Aldrich, Acrös, Fluka) and used as received.

1D NMR (^{1}H, ^{13}C-{^{1}H}, 13C-{1H} APT) and 2D NMR (COSY, NOESY, HSQC) spectra were recorded on Bruker Advance II+ 300 and 400 MHz (UltraShield Magnet), at ambient temperature. ^{1}H and ^{13}C chemical shifts (δ) are

expressed in ppm relative to Me$_4$Si. Coupling constants (J) are given in Hz and multiplicities are presented as: br (broad), s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), sept (septet) and m (multiplet).

Crystals suitable for single-crystal X-ray analysis were grown as described in the synthetic procedures. Crystallographic data were collected at *Instituto Superior Técnico* by Dr. Sónia Barroso. Crystals of air/moisture sensitive compounds were selected inside the glovebox, covered with polyfluoroether oil and mounted on a nylon loop. The data were collected using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS.[56] The structures were solved and refined using direct methods with programs SIR2004 or SHELXS-97.[57–59] All programs are included in the package of programs WINGX-Version 1.80.01 SHELXL.[60,61] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. The molecular diagrams were drawn with ORTEP-3 for Windows, included in the software package.[62] Selected crystallographic experimental data and structure refinement parameters are presented in Table 7.

Table 7: Selected crystallographic experimental data and structure refinement parameters for 3 and 7.

	7	3
Empirical formula	TiC$_{34}$H$_{54}$Cl$_2$N$_2$O$_2$	VC$_{40}$H$_{65}$N$_2$O$_4$
Formula weight	641.59	688.88
Temperature (K)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
V(Å^3)	3567.3(4)	7823.8(7)
a(Å)	16.6997(11)	15.5180(11)
b(Å)	15.6387(10)	23.5210(10)
c(Å)	15.1741(10)	21.8270(10)
α(°)	90	90
β(°)	115.821(2)	100.875(2)
γ(°)	90	90
Z, ρ_{calc} (gcm^{-3})	4, 1.195	8, 1.170
μ(mm^{-1})	0.420	0.293
Crystal size	0.04×0.18×0.18	0.20×0.20×0.30
Crystal colour	orange	brown
Crystal shape	plate	block
Refl. collected	15403	48641
Unique refl. [R(int)]	6299 [0.0811]	24929 [0.0490]
R1 [I>2σ(I)]	0.0608	0.0495
wR2 [I>2σ(I)]	0.1292	0.0967
GooF	0.936	1.000
Flack's param.		-0.003(12)

Synthetic Procedures

Synthesis of 6,6'-(2-(dimethylamino)ethylazanediyl)bis(methylene)bis(2, 4-di-tert-butylphenol), H2L1, 1.[21]

A solution of 2,4-di-tert-butylphenol (5,0 g, 24,2 mmol), N,N-dimethylethylenediamine (1,4 mL, 12,3 mmol), and 36% aqueous formaldehyde (2,5 mL, 33,6 mmol) in methanol (10 mL) was stirred at room temperature for 3 days. The mixture was cooled to -4 ºC overnight and a precipitate formed. The solution was filtered off and the solid was thoroughly washed with ice cold methanol to give a white powder. Yield: 3.7 g, 58%. The compound was further purified by recrystallization from methanol.

^{1}H NMR (300 MHz, CDCl$_3$, ppm): 9.81 (br, 2H, O*H*), 7.19 (d, $^4J_{HH}$ = 2.1 Hz, 2H, o- C*H*-Ar), 6.87 (d, $^4J_{HH}$ = 2.0 Hz, 2H, p-C*H*-Ar), 3.60 (br, 4H, NC*H*$_2$Ar), 2.59 (s, 4H,

NC*H*$_2$CH$_2$N), 2.31 (s, 6H, N(C*H*$_3$)$_2$), 1.39 (s, 18H, C(C*H*$_3$)$_3$), 1.27 (s, 18H, C(C*H*$_3$)$_3$).

Synthesis of (S)-6,6'-((1-ethylpyrrolidin-2-yl)methylazanediyl)bis(methylene)- bis(2,4-di-tert-butylphenol), H$_2$L^2, 2.[41]

A solution of 2,4-di-tert-butylphenol (4,13 g, 20,00 mmol), (S)-ethylpyrrolidine (1,35 mL, 12,30 mmol), and 36% aqueous formaldehyde (1,65 mL, 22,00 mmol) in methanol (10 mL) was stirred at room temperature for 3 days. The mixture was cooled to -4 ºC overnight leading to the formation of a sticky precipitate. The supernatant solution was decanted and the solid was redissolved in MeOH. Upon cooling the compound precipitate out of solution. The solid was separated by filtration and washed thoroughly with ice cold methanol to give an off-white solid. Yield: 1.70 g, 30%. The compound was further purified by recrystallization from methanol.

^{1}H NMR (300 MHz, CDCl3, ppm): 9.69 (br, 2H, O*H*), 7.20 (d, $^4J_{HH}$ = 2.2 Hz, 2H, C*H*-Ar), 6.87 (d, $^4J_{HH}$ = 2.2 Hz, 2H, C*H*-Ar), 3.87 (d, $^2J_{HH}$ = 13.3 Hz, 2H, ArC*H*$_2$N), 3.43 (d, 2H, $^2J_{HH}$ = 13.2 Hz, ArC*H*$_2$N), 3.35 (m, 1H, C*H*$_2$), 3.04 (m, 1H, C*H*$_2$CH$_3$), 2.66 (m, 2H, C*H*$_2$ + C*H*), 2.48 (m, 1H, NC*H*$_2$), 2.25 (m, 2H, C*H*$_2$CH3 + C*H*$_2$), 1.90 (m, 1H, C*H*$_2$), 1.68 (m, 2H, C*H*$_2$), 1.48 (m, 1H, C*H*$_2$), 1.39 (s, 18H, C(C*H*$_3$)$_3$), 1.27 (s, 18H, C(C*H*$_3$)$_3$), 1.20 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH$_2$C*H*$_3$).

Reaction of H$_2$L^2 with VOCl$_3$.

A solution of **H$_2$L^2** (0,57 g, 1 mmol) in THF was slowly added to NaH (0,056 g, 2,2 mmol) and the mixture was stirred for 2 h at 50ºC in inert atmosphere. The colorless solution was cooled to room temperature and VOCl$_3$ (0,095 ml, 1 mmol) was slowly added to it. The dark blue reaction mixture was stirred overnight and then evaporated under reduced pressure to give a greenish solid (0,329 g).

Synthesis of [VOL^2(O^{i}Pr)], 3.

A solution of **H$_2$L^2** (0,57 g, 1 mmol) in 5 ml THF was prepared under inert atmosphere, and VO(OiPr)$_3$ (0,24 ml, 1 mmol) was slowly added to it. The mixture was stirred overnight, and then the solvent was evaporated under reduced pressure. The resulting dark brownish product was extracted in diethyl ether and again evaporated and dried under reduced pressure (η=60%).

Dark brown crystals suitable for X-ray diffraction were obtained from a toluene/hexane mixture at -4ºC.

^{1}H NMR (300 MHz, CDCl3, ppm): 7.38 (d, $^4J_{HH}$ = 2.4 Hz, 1H, C*H*-Ar), 7.21 (d, $^4J_{HH}$ = 2.5 Hz, 1H, C*H*-Ar), 7.16 (d, $^4J_{HH}$ = 2.4 Hz, 1H, C*H*-Ar), 6.91 (d, $^4J_{HH}$ = 2.31H, C*H*-Ar), 4.91 (d, $^2J_{HH}$ = 15.3 Hz, 1H, ArC*H*HN), 4.26 (d, 1H, $^2J_{HH}$ = 12.3 Hz, ArC*H*HN), 3.93 (m, 1H, C*H*$_2$), 3.64 (d, $^2J_{HH}$ = 15.3 Hz, 1H, ArC*H*HN), 3.42 (m, 1H, NC*H*(CH$_2$)$_2$), 3.16 (d, 1H, $^2J_{HH}$ = 12.2 Hz, ArC*H*HN), 3.00 (m, 1H, C*H*$_2$CH$_3$), 2.81 (m, 2H, C*H*$_2$), 2.24 (m, 1H, C*H*$_2$), 1.83 (m, 4H, C*H*$_2$ + C*H*$_2$), 1.39 (d, $^2J_{HH}$= 6.1, 3H, OC(C*H*$_3$)$_3$), 1.49 (s, 9H, C(C*H*$_3$)$_3$), 1.47 (d, 3H, OC(C*H*$_3$)$_3$) 1.45 (s, 9H, C(C*H*$_3$)$_3$), 1.35 (s, 9H, C(C*H*$_3$)$_3$), 1.26 (s, 9H, C(C*H*$_3$)$_3$), 1.13 (m, 3H, CH$_2$C*H*$_3$).

EA calculated for C$_{40}$H$_{65}$N$_2$O$_4$V·0.5(C$_7$H$_8$): C, 64.83; H, 8.63; N, 3.48. Found: C, 64.59; H, 8.78; N, 3.64.

Synthesis of [Ti^{III}L^{1}Cl(THF)], 4.[40]

A solution of **H$_2$L^1** (1.05 g, 2.00 mmol) in THF was added to NaH (0.11 g, 4.40 mmol) and the mixture was stirred for 2 h at 50ºC. The colorless solution obtained was allowed to cool down to room temperature, filtered through celite and added to a suspension of TiCl$_3$(THF)$_3$ (0.74 g, 2.00 mmol) in THF at -80ºC. The mixture was allowed to reach room temperature slowly and stirred overnight. The yellow/orange solution obtained was evaporated to dryness and the residue was extracted in Et$_2$O and filtered. Evaporation of the solution led to a microcrystalline yellow/orange solid, which was filtered from the orange solution. Yield: 0.52 g, 38%.

Synthesis of [Ti^{IV}L^{1}Cl]$_2$(μ-O), 5.[42]

A solution of **4** (0,52 g, 0,8 mmol) in THF was exposed to air, through a CaCl$_2$ drying tube, for 12 h. The red/orange solution obtained was evaporated to dryness, and the residue was extracted with Et$_2$O and filtered. Evaporation of the Et$_2$O solution to dryness led to an orange crystalline solid. Yield: 0,40 g, 85%.

^{1}H NMR (300 MHz, C$_6$D$_6$, ppm): 7.47 (s, 4H, p-CH-Ar), 7.11 (s, 4H, o-CH-Ar), 5.77 (d, 4H, $^2J_{HH}$ = 13.7 Hz, NCH_2Ar), 3.30 (d, 4H, $^2J_{HH}$ = 13.8 Hz, NCH_2Ar), 2.25 (m, 4H, CH_2), 1.90 (s, 12H, N(CH_3)$_2$), 1.46 (m, 4H, CH_2), 1.44 (s, 36H, C(CH_3)$_3$), 1.36 (s, 36H, C(CH_3)$_3$).

Synthesis of [TiL^1(OiPr)$_2$], 6.

Method 1: From [Ti^{IV}L^{1}Cl]$_2$(μ-O).

Triethylamine (0.22 mL, 1.6 mmol) was added to a solution of **5** (0,5 g, 0.4 mmol) in isopropanol and the mixture was stirred for 48 h. The orange-yellow solution obtained was evaporated to dryness, and the residue was extracted in Et$_2$O and filtered. Evaporation of the Et$_2$O solution under vacuum led to an orange powder.

Method 2: From Ti(O^{i}Pr)$_4$.

A solution of Ti(O^{i}Pr)$_4$ 1M in Toluene was prepared and added (3 ml, 3 mmol) to a THF solution of **H$_2$L^1** (1,574 g, 3 mmol). The mixture was stirred for 2 hours and the yellow solution obtained was evaporated and dried under reduced pressure. The product was then extracted in toluene and again evaporated to dryness. Yield: 1,86 g, 96%.

^{1}H NMR (300 MHz, C$_6$D$_6$, ppm): 7.58 (d, 2H, $^4J_{HH}$ = 2.3 Hz, p-CH-Ar), 7.06 (d, 2H, $^4J_{HH}$ = 2.1 Hz, o-CH-Ar), 5.23 (sept, $^3J_{HH}$ = 5.9 Hz, 1H, CH(CH$_3$)$_2$), 4.81 (sept, $^3J_{HH}$ = 5.9 Hz, 1H, CH(CH$_3$)$_2$), 4.24 (d, 2H, $^2J_{HH}$ = 13.1 Hz , NCH_2Ar), 3.12 (d, 2H, $^2J_{HH}$ = 13.1 Hz, NCH_2Ar), 2.28 (m, 2H, NCH_2CH$_2$NMe$_2$), 2.09 (s, 6H, N(CH_3)$_2$), 1.81 (m, 2H, NCH$_2$CH_2NMe$_2$), 1.76 (s, 18H, C(CH_3)$_3$), 1.50 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH(CH_3)$_2$), 1.43 (s, 18H, C(CH_3)$_3$), 0.98 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH(CH_3)$_2$).

Synthesis of [TiL^{1}Cl$_2$], 7.[42]

To a solution of **6** (1,86 g, 3 mmol) in CH$_2$Cl$_2$, TMSCl in great excess (0,84 ml, 6,6 mmol) was slowly added. The mixture was stirred overnight and the dark orange solution obtain evaporated to dryness. The product was then extracted in Toluene and evaporated to dryness under vacuum to give a reddish-orange powder. Yield: 1,60 g, 89%. Dark orange crystals suitable for X-ray diffraction were obtained from toluene at -4ºC.

^{1}H NMR (300 MHz, C$_6$D$_6$, ppm): 7.59 (d, 2H, $^4J_{HH}$ = 2.3 Hz, p-CH-Ar), 6.97 (d, 2H, $^4J_{HH}$ = 2.3 Hz, o-CH-Ar), 4.35 (d, $^2J_{HH}$ = 13.8 Hz, 2H, NCH_2Ar), 2.79 (d, $^2J_{HH}$ = 13.3 Hz, 2H, NCH_2Ar), 2.14 (m, 2H, CH_2), 1.94 (s, 6H, N(CH_3)$_2$), 1.80 (s, 18H, C(CH_3)$_3$), 1.61 (m, 2H, CH_2), 1.39 (s, 36H, C(CH_3)$_3$).

EA calculated for C$_{34}$H$_{54}$Cl$_2$N$_2$O$_2$Ti·0.5(C$_7$H$_8$): C, 65.51; H, 8.50; N, 4.07. Found: C, 65.47; H, 8.67; N, 3.83.

General Procedure for the catalytic pinacol coupling reactions.

A solution of the [Ti^{IV}] complex (in adequate proportion) in THF was prepared in a vial inside the glovebox. The metallic reductant (6 mmol) and TMSCl (0,28 ml, 3 mmol) were sequentially added. The mixture was stirred for 10 minutes and benzaldehyde (0,20 ml, 2 mmol) was added. The vial was sealed and brought outside the glovebox, where the reaction stirred overnight at the appropriate temperature. After 16 hours of reaction, the vial was opened to air and the reaction quenched with 5 ml of an aqueous 5% Na$_2$CO$_3$ solution. The mixture was filtered and extracted with 3x15 ml of ethyl acetate, which was then evaporated at reduced pressure. The crude obtain was stirred with 5 ml of a HCl solution 1M in THF for 2 hours at room temperature, diluted with 10 ml distilled water and, again, extracted in 3x15 ml

ethyl acetate and evaporated to dryness under vacuum. An NMR sample of the product was taken in CDCl$_3$.

Preparation of sample for EPR spectra

To a small deareated vial with Zinc powder (0,390 g, 6 mmol) a solution of 5% [Ti^{IV}L^{1}Cl]$_2$(μ-O) in 4 ml THF was added. TMSCl (0,28 ml, 3 mmol) was then added and, after 5 minutes stirring, the first aliquot was taken. Benzaldehyde (0,20 ml, 2 mmol) was then added and the second aliquot immediately taken. The aliquots were frozen until the EPR spectra were taken.

Reaction of 4 with benzaldehyde.

A solution of benzaldehyde 1:100 in THF was prepared in the glovebox, and 0,2 ml (0,02 mmol) of that solution were added to crystalline **4** (15 mg, 0,02 mmol) in the same solvent in a J-Young NMR tube. The mixture was left to react for two days inside the glovebox, after which the solvent was evaporated under vacuum and the products redissolved in CDCl$_3$.

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