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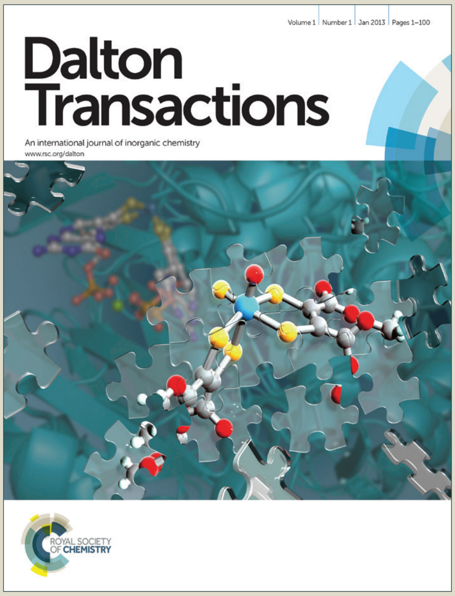

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Imido-Pyridine Ti(IV) Compounds: Synthesis of Unusual Imido-Amido Heterobimetallic Derivatives

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S. Pedrosa,[a] F. Vidal,[a,c] Lucia Myongwon Lee,[b] I. Vargas-Baca,[b] P. Gómez-Sal[a,*] and M. E. G. Mosquera[a,*]

The reaction of lithiated picolines and [TiCl$_3$(η^5-C$_5$Me$_5$)] leads to several bridging or terminal imido compounds, each of which can be selectively formed by control of stoichiometry and temperature. Specifically, the dinuclear imido-bridged [TiCl(η^5-C$_5$Me$_5$)(μ-NR)]$_2$ (**1a**, NR = 2-imido-3-picoline; **1b**, NR = 2-imido-5-picoline) species and the unusual Ti-Li imido-amido heterobimetallic complex [{Li(THF)}{[Ti(η^5-C$_5$Me$_5$)(NR)(NHR)$_2$}] (**2a**, NR = 2-imido-3-picoline; **2b**, NR = 2-imido-5-picoline) were isolated. Compounds **2** are in effect the first structurally characterized examples of titanium(IV) coordinated to terminal imido-pyridines. DFT-D calculations for **2a** denote a multiple bond character between titanium and the imido ligand and a strong polarization of electron density by the alkali cation in spite of the lack of intermetallic bonding.

Introduction

Even though imido metal-complexes have been known for decades, they still arise great interest due to their remarkable structures and reactivity.[1] The importance of these compounds to organic synthesis and catalysis in laboratory and industrial scale is well known.[2] For example, imido moieties act as auxiliary ligands in catalysts for ring-opening metathesis,[3] and imido derivatives are involved in the commercial production of acrylonitrile by ammoxidation of propylene.[4] In particular, imido titanium complexes display interesting reactivity towards many unsaturated organic substrates, leading to the formation of new organic and organometallic compounds.[5,6] The potential for activation of small molecules such as CO$_2$ is a particularly attractive aspect of titanium imido chemistry.[7] Indeed, it has recently been shown that the unsaturated 12/14 electron complexes [Ti(N^{t}Bu)Cl$_2$Py$_2$] and [Ti(NPh(2,6-^{i}Pr)$_2$)Cl$_2$Py$_3$] quantitatively react with CO$_2$ yielding a symmetrical urea in mild conditions.[8] Moreover, the role of transition metal imido derivatives in olefin polymerization processes has been widely explored.[9]

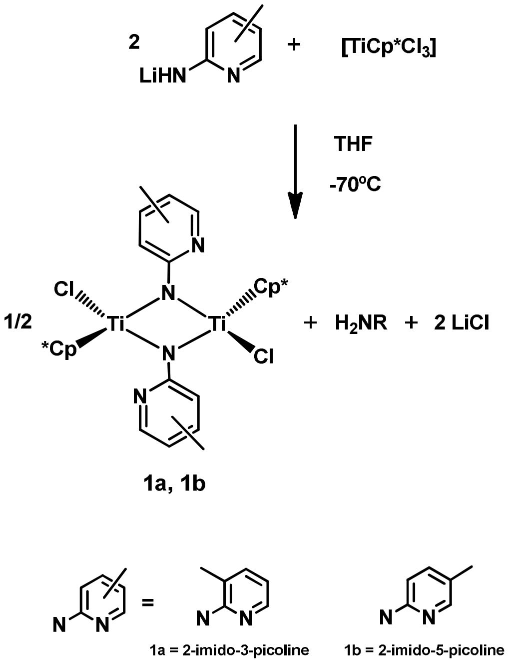
The presence of two different metal ions in the same amido/imido complex elicits valuable synergistic effects in processes of synthetic interest.[10] For instance, a recent study has pointed out the role of the Hf(IV)-pyridylamido/ER$_n$ heterometallic transient species (ER$_n$ = ZnR$_2$ or AlR$_3$) in polymerization of 1-hexene.[11] Our approach to the formation of heterometallic imido species combines titanium and lithium. Apart from the intrinsic interest of species bearing two metals of very different nature, an electropositive alkali metal and a transition element, such Ti-Li heterometallic species could provide the gateway to the generation of other heterometallic species by metathesis with salts of other metals.

As ligand precursors, we chose functionalized amines because we are interested in the effect of the second functional group on their coordination behavior and reactivity.[12] In this report, we present the results of using amino-picolines, aiming to obtain imido-pyridine metal derivatives. The presence of the pyridine group in the ligand would help to stabilize the coordination spheres and confer attractive electronic properties to the complexes. In fact, related species —such as the amidopyridine compounds developed by Dow/Symyx— have unique abilities in olefin polymerization.[13] Despite the interesting behavior expected from any amido or imido-pyridine derivatives,[14] there is a surprising paucity of such species reported for titanium.[15-19]

Here we describe the synthesis, characterization and computational studies of Ti(IV) compounds that contain imido-pyridine ligands. In the course of these investigations we observed different results depending on the stoichiometry and the temperature used for the synthesis. By controlling those factors, the formation of the dinuclear imido-bridge [TiCl(η^5-C$_5$Me$_5$)(μ-NR)]$_2$ (**1**) species and the unusual Ti-Li imido-amido heterometallic derivatives [{Li(THF)}{[Ti(η^5-C$_5$Me$_5$)(NR)(NHR)$_2$}] (**2**) was selectively achieved. The electronic structure of **2** was examined to probe the effect of the alkali metal ion. We also propose a mechanism to account for the outcome of the synthesis reactions.

Results and discussion

Synthesis of the Ti(IV) complexes. The proligands 2-amino-3-picoline and 2-amino-5-picoline were deprotonated with an equimolecular amount of ^{n}BuLi, a change from colorless to yellow solution was indicative of the formation of the LiNHR lithium amides. The titanium precursor [$TiCl_3(\eta^5-C_5Me_5)$] was added, turning the solution red. The reactions were carried out in THF because the mixture components are not soluble in hydrocarbons such as toluene. We studied the reaction in two different stoichiometries. Initially the reaction was carried out in a 1:2 ([$TiCl_3(\eta^5-C_5Me_5)$] to LiNHR) ratio which led to the dinuclear imido bridged species [TiClCp*(μ-NR)]$_2$ (**1a**, NR = 2-imido-3-picoline; **1b**, NR = 2-imido-5-picoline) as the final product (scheme 1).

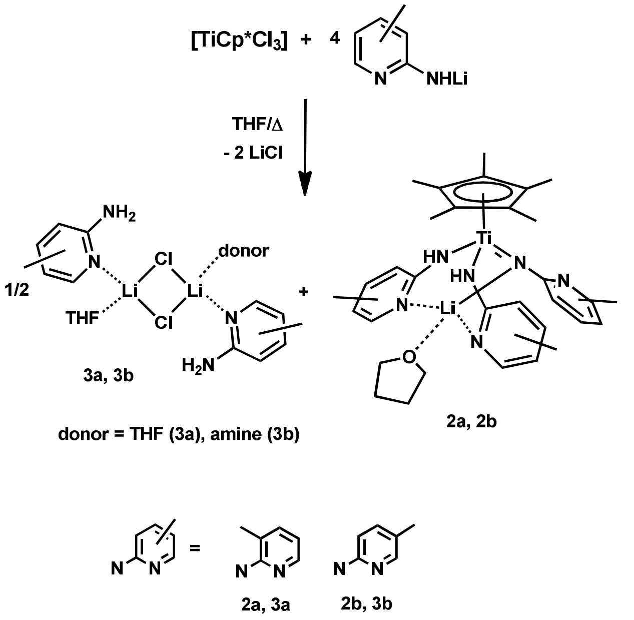


Scheme 1. Synthesis of compounds **1a-b**

Compounds **1a-b** were isolated and characterized by ^{1}H NMR spectroscopy. In their proton spectra, only one set of signals for the aromatic protons of the ligands was observed and no resonance from the NH groups was present, indicating the deprotonation of the amido precursors to generate the imido ligands. $^{13}C\{^1H\}$ NMR data were not acquired due to the low solubility of compounds **1a-b**. The structure **1b** was confirmed by single-crystal X-ray diffraction.

Many peaks were observed in the ^{1}H NMR spectrum of the reaction mixture during the initial stages likely due to mixed amido-imido intermediates that could not be unequivocally unidentified. As the reaction proceeds, complexes **1a-b** emerged as the most abundant products. Signals characteristic of amino protons (4.59 ppm for 2-amino-3-picoline and 4.37 ppm for 2-amino-5-picoline) were observed indicating that free amine was generated as a by-product. Compounds **1a-b** could also be obtained when other *s*-block organometallic reagents were used as bases, for example $MgBu_2$ was used to deprotonate the amino picolines, following Power's method.[20] In fact, the imido reagent [MgNR]$_n$ provided a better route to obtain **1a-b**, the corresponding ^{1}H NMR spectra demonstrated that the Ti(IV) imido derivatives **1a-b** were formed more rapidly and in higher yield.

When the reaction was carried out using a 1:4 ([$TiCl_3(\eta^5-C_5Me_5)$] to LiNHR) ratio and at higher temperature (under reflux), the final result was different. In this case, not only the substitution of all chloro ligands was attained, but also one amido ligand was deprotonated leading to the unusual bimetallic species [Li(THF)][Ti((η^5-C_5Me_5)(NR)(NHR)$_2$]$_2$ (**2a**, NR = 2-imido-3-picoline; **2b**, NR = 2-imido-5-picoline).

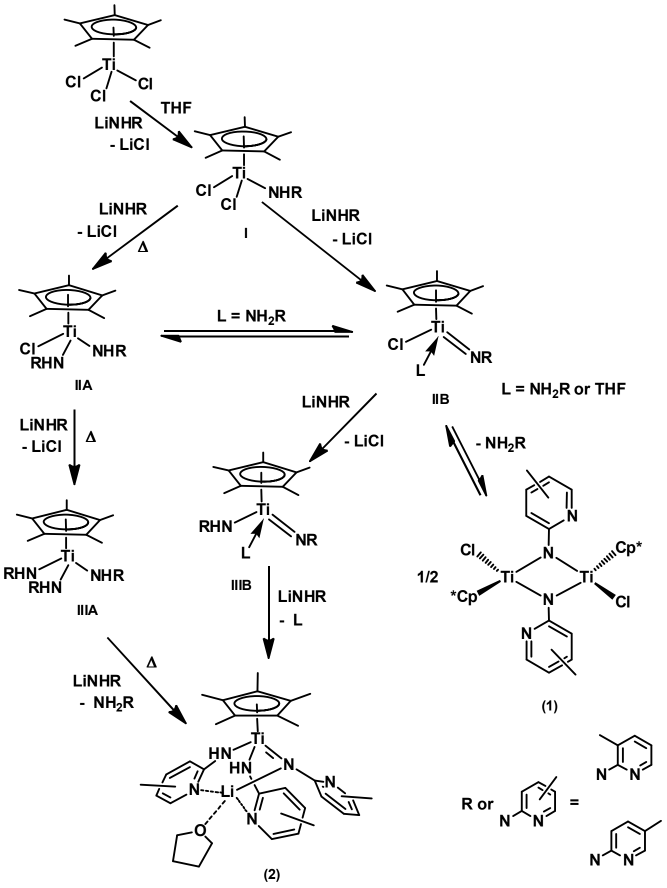


Scheme 2. Synthesis of compounds **2a-b.**

Complexes **2a-b** were characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. In their spectra, signals characteristic of the proton of the amido groups (4.29 and 4.25 ppm for **2a** and **2b**, respectively) were evident and two sets of aromatic signals were observed with intensity ratio 2:1, which corresponds to the two distinct types of ligand, amido and imido, in the proposed structure of these products. The structure of **2a** was confirmed by single-crystal X-ray diffraction. The derivatives **3**, identified by X-ray diffraction, were isolated from the mother liquor of crystallization of compounds **2**.

Proposed mechanism. A sequence of steps that would explain the formation of **1** or **2**, depending on the reaction conditions, is shown in Scheme 3. The first step in this proposal is the formation of [$TiCl_2$Cp*(NHR)] (I) upon substitution of one chloride ligand by the amido group of LiNHR. The second step could be the substitution of another chloride ion by reaction with a second molecule of LiNHR to give the diamido intermediate [TiClCp*(NHR)$_2$] (IIA). However, it is also possible that the lithium amide abstracts the proton of the amido ligand forming the terminal imido intermediate [TiClCp*(=NR)(L)] (L = THF or NH_2R) (IIB), such intermediate would be stabilized by a donor ligand such as NH_2R -generated *in situ*- or the solvent. ^{1}H NMR spectroscopy alone could not distinguish between these alternative pathways because the two products could easily be in equilibrium, in fact such a proton-transfer process has been observed for related amido-imido species.[21]

However, each intermediate would impact the outcome in a different way. The imido complex IIB could quickly dimerize to give the imido bridged species [TiClCp*(μ-NR)]$_2$ (**1**), as described for related systems.[21] While their low solubility facilitates isolation of complexes **1**, this property could also significantly impact the evolution of the reaction. Indeed, the formation of imido ligands from amines often involves multiple species, one of which is eventually selected by kinetics or solubility.[21]



Scheme 3. Proposed mechanism for the formation of **1** and **2.**

Alternative to dimerization, IIB could undergo stepwise reaction with two equivalents of LiNHR forming first the amido-imido intermediate [TiCp*(=NR)(NHR)(L)] (IIIB) and finally displacement of L would yield the heterometallic product **2**. In contrast, IIA would react with LiNHR to give the triamido intermediate [TiCp*(NHR)$_3$] (IIIA); this in turn would be deprotonated to give **2** only.

A shift towards dissociation in the equilibrium between IIB and **1** at reflux temperature would explain the conditions in which the bimetallic species **2** were formed. The ability of lithium amides as deprotonating agent has been suggested also in the formation of other amido-imido titanium species.[23,24] As well, the isolation in the reaction media of the amines as LiCl adducts, {[Li(μ-Cl)]$_2$·(NH$_2$R)$_2$(THF)$_2$} (**3a**) and {[Li(μ-Cl)]$_2$·(NH$_2$R)$_3$(THF)} (**3b**), support the proposed roles for LiNHR in this mechanism. We finally note that only **2a,b** were isolated in low yield from the reaction of [TiCl$_3$(η^5-C$_5$Me$_5$)] with 3 equivalents of LiNHR; and that attempts to further deprotonate **2** with more excess LiNHR were unsuccessful. As well efforts to isolate I species by performing the reaction of [TiCl$_3$(η^5-C$_5$Me$_5$)] with one equivalent of LiNHR led to mixtures where only small amounts of compounds **1a,b** could be identified.

X-Ray diffraction. As shown in Figure 1, **1b** is centrosymmetric and presents a dinuclear structure where the imido ligands bridge the titanium atoms. Only one other titanium μ-pyridylimido has been structurally characterized.[15] In **1b**, a Ti$_2$N$_2$ core is observed. The influence of the pyridinic nitrogen on the coordination geometry around the metal is clear. As such, while this kind of species usually shows a tetrahedral environment around the metal atom,[22] in this case the coordination geometry is a square-based pyramid, where the atoms Cl1–N1–N1(A)–N2 define a plane at a 1.1161(9) Å distance from the titanium. Also, the bridge is not symmetric; the longer Ti-N distance corresponds to the bridging imido bond whose pyridinic nitrogen is coordinated to the titanium atom.

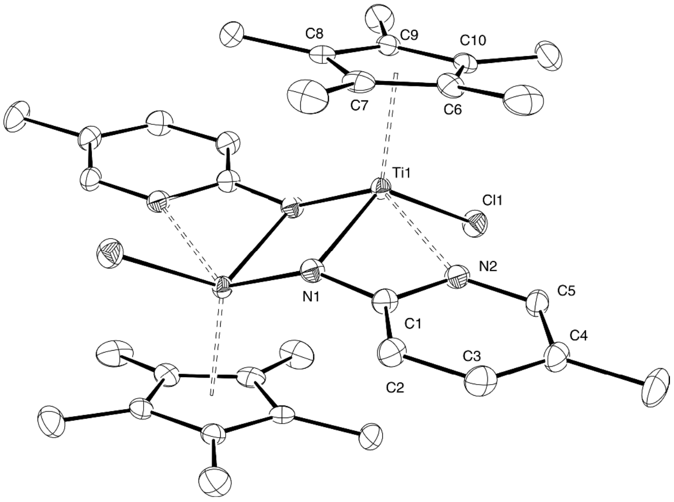


Figure 1. Molecular structure for **1b**, (ellipsoids of 30% of probability). Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [deg] for **1b** and **2a.**

1b			
Bond lenghts [Å]		**Angles [deg]**	
Ti1–Ti1(A)	3.003(2)	Ti1–N1–Ti1(A)	97.48(16)
Ti1–N1	2.131(4)	N1–Ti1–N1(A)	82.52(16)
Ti1–N1(A)	1.857(4)	N1–Ti1–Cl1	128.17(11)
Ti1–N2	2.229(4)	Ti1–N1–C1	94.9(3)
Ti1–Cp*	2.066(1)	Ti1(A)–N1–C1	151.3(3)
N1–C1	1.368(6)		
Ti1–Cl1	2.354(2)		
2a			
Bond lenghts [Å]		**Angles [deg]**	
Ti(1)-N(1)	1.763(4)	Ct-Ti(1)-N(1)	120.05
Ti(1)-N(3)	2.033(4)	Ct-Ti(1)-N(3)	109.39
Ti(1)-N(2)	2.045(4)	Ct-Ti(1)-N(2)	112.83
Ti(1)-Ct	2.084	Ti(1)-N(1)-C(11)	156.5(3)
Ti(1)-Li(1)	2.902(8)	Ti(1)-N(3)-C(31)	138.9(3)
O(1)-Li(1)	1.958(9)	Ti(1)-N(2)-C(21)	129.5(3)
N(1)-Li(1)	2.127(9)	N(1)-Ti(1)-N(3)	104.43(17)

N(6)-Li(1)	2.026(9)	N(1)-Ti(1)-N(2)	103.74(16)
N(5)-Li(1)	2.052(9)	N(3)-Ti(1)-N(2)	104.10(16)
		O(1)-Li(1)-N(1)	110.6(4)

Symmetry transformations used to generate equivalent atoms: Compound **1b**: (A) –x+1, -y, -z+2.

The molecular structure of **2a** is shown in Figure 2. The titanium atom is in a pseudo tetrahedral environment; one coordination position is occupied by the Cp* ring, two by the amido ligands and the fourth by the imido ligand. Such a "piano stool" structure is typical of monocyclopentadienyl complexes. An important feature of this structure is the coordination of a lithium atom; four other imido compounds containing both metals[23,25,26] are known but none with a heterocylic imido ligand. The lithium center is bound to two pyridinic nitrogens from the amido ligands. The tetrahedral coordination sphere of lithium is completed by the THF molecule and the bond to the imido ligand.

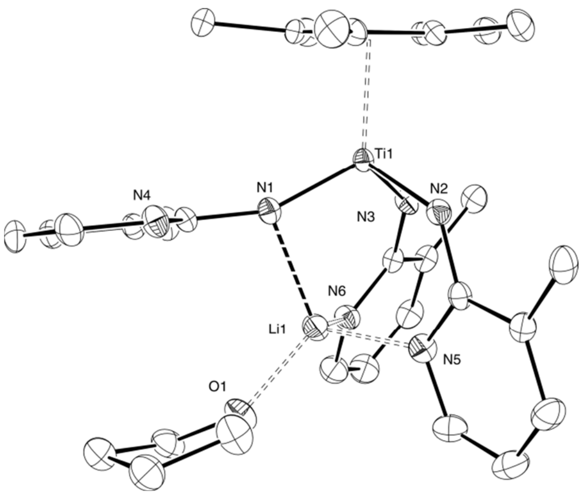


Figure 2. Molecular structure of **2a.** Ellipsoids of 30% of probability. Hydrogen atoms are omitted for clarity.

The Ti-N$_{amido}$ bond lengths (2.033(4) and 2.045(4) Å) are very similar to those found in the structure of Li[(η^5-Cp*)Ti=N^{t}Bu)(NH^{t}Bu)$_2$][23] and fall within the typical range for this type of interaction. As well, the Ti-N-C angles around the N$_{amido}$ (129.5(3) and 138.9(3)º for N(2) and N(3) respectively) are within the values reported and correspond to a *sp*^{2} hybridization.

The metal-imido bond distance Ti(1)-N$_{imido}$(1) 1.763(4) Å is longer than the ones found in the analogous imido-amido titanium derivatives of the type {Ti(NHR)(NR)} described which range from 1.670 to 1.752.[23-25, 26a,27] However, the angle Ti(1)–N$_{imido}$(1)-C$_{ipso}$(11) in **2a** is clearly smaller, 156.5(3)º, than the ones previously reported that are closer to 180º, typical of *sp* hybridization. In fact, for 95% of the imido titanium species reported (out of 275 observations), the value for this angle falls in the range 163.54-180.00º.[28] The presence of an interaction between the N$_{imido}$ and the lithium atom could be responsible for this geometrical feature. This unusual interaction corresponds to the longest N-Li bond distance in the molecule, 2.127(9) Å; the Li-N$_{py}$(5) and Li-N$_{py}$(6) distances are 2.052(9) and 2.026(9) Å, respectively. Because the last two cases clearly correspond to coordination bonds, the longer Li-N$_{imido}$(1) bond distance is suggestive of charge separation in **2a** where the negative charge would be centered on the N$_{imido}$ and the positive on the lithium atom. Interestingly, the N$_{imido}$-Li distance in **2a** is also longer than in the other two reported titanium imido compounds, 2.092 Å[25] and 2.071 Å.[26a] Another intriguing feature of the **2a** structure is the short distance between Ti(1) and Li(1) (2.902(8) Å, cf. the sum of covalent radii 2.88 Å[29]) which indicates that the possibility of an intermetallic bond cannot be excluded, in spite of the apparent absence of valence electrons in both atoms.

Finally, in derivatives **3**, the coordination sphere of the Li is also stabilized by the interaction with the pyridinic nitrogen. These two compounds consist of Li$_2$Cl$_2$ cores solvated by either the amine or THF molecules. For **3a**, in the unit cell two different LiCl solvates are present, [LiCl(THF)(NRH$_2$)]$_2$ and [LiCl(THF)$_2$]$_2$. Very few other LiCl solvates with pyridine groups have been reported and none as a co-crystal with [LiCl(THF)$_2$]$_2$.[30-31] In **3b** the lithium atoms show different environments, Li(1) is coordinated to one THF and one amine, while Li(2) is coordinated to two amine molecules.

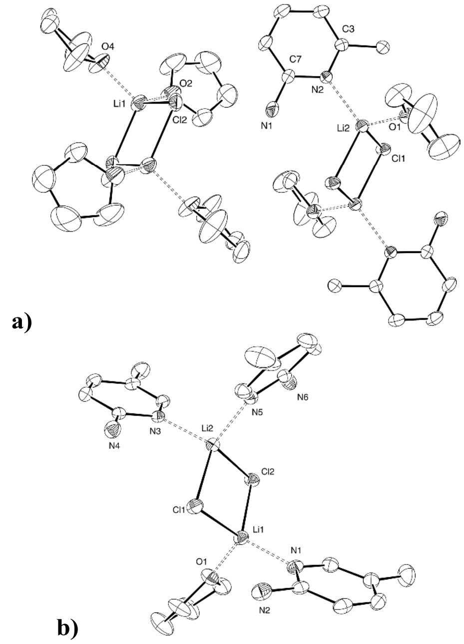


Figure 3. Molecular structure of **3a** (a) and **3b** (b), ellipsoids of 30% of probability. Hydrogen atoms are omitted.

Table 2. Selected bond lengths [Å] and angles [deg] for **3a-b.**

3a			
Bond lengths [Å] and Angles [deg]			
Li(1)-O(3)	1.962(7)	Li(2)-N(2)	2.122(5)
Li(1)-O(2)	1.960(7)	Li(2)-Cl(1)	2.402(5)
Li(1)-Cl(2)#1	2.369(7)	Li(2)-Cl(1)#2	2.350(5)
Li(1)-Cl(2)	2.341(7)	Cl(2)#2-Li(1)-Cl(2)	101.0(2)
Li(2)-O(1)	1.988(5)	Cl(1)-Li(2)-Cl(1)#2	100.7(2)
3b			
Bond lengths [Å] and Angles [deg]			
Li(1)-O(1)	1.916(7)	Li(2)-N(5)	2.030(7)

Li(1)-N(1)	2.045(7)	Li(2)-Cl(1)	2-386(6)
Li(1)-Cl(1)	2.370(6)	Li(2)-Cl(2)	2.363(6)
Li(1)-Cl(2)	2.338(6)	Cl(2)-Li(1)-Cl(1)	102.1(2)
Li(2)-N(3)	2.025(6)	Cl(2)-Li(2)-Cl(1)	100.9(2)

Symmetry transformations used to generate equivalent atoms: Compound **3a**: #1 -x,-y+2,-z ; #2 -x+2,-y+2,-z+1

Computational investigations. For compound **2a**, DFT-D calculations (ADF,[32] B3LYP-D3,[33,34] TZ2P, ZORA[35]) were employed to probe the possibility of a Ti(1)-Li(1) interaction and to study the details of the bonding between the imido nitrogen and the two metal ions.

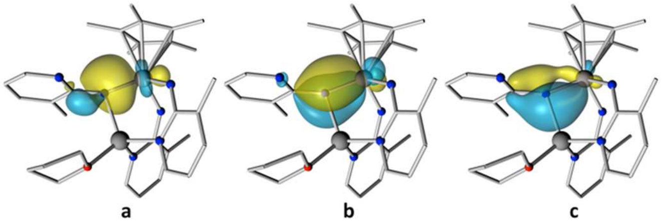


Figure 4. Boys-Foster localized molecular orbitals (LMO, ϕ_i) for the Ti-N$_{imido}$ bond of **2a.** a) sigma: ϕ_{150} - $\phi_{152;}$ pi: ϕ_{150} + $\phi_{152;}$ c) pi: ϕ_{155}. Isosurfaces plotted at 0.03 a.u

The experimental molecular structure was satisfactorily reproduced by geometry optimization. The RMS deviations for most calculated distances fall within the usual ranges: C-C (0.012 Å), C-O (0.003 Å), C-N (0.015 Å), and Ti-C,N (0.016 Å). A somewhat larger RMS deviation (0.050 Å) was obtained for the Li-N,O distances. No significant conformational differences were observed by comparing the model with the crystallographic result.

The Kohn-Sham molecular orbitals derived from SCF calculations are naturally delocalized throughout the molecule and each cannot be attributed to any pair of atoms in particular. The bonding analysis was therefore carried out with the Boys-Foster[36] method for the construction of localized molecular orbitals (LMOs); the sigma and pi 2*p*-3*d* interactions of the classical bonding description for a metal-imido bond could be identified in LMO 155 and the linear combinations of LMOs 150 and 152 (Figure 4). In contrast, no significant contribution of the atomic 1*s* orbital of Li^+ to any occupied molecular orbital could be found. Calculated Voronoi[37] charges for all the pyridinic nitrogens are similar to each other (-0.18 a.u. to -0.22 a.u.) and to those of N(2) and N(3) (both -0.26 a.u.) but less negative than the -0.40 a.u. calculated for N(1), the imido nitrogen. The overall ligand charges also indicate that the doubly-deprotonated ligand bears most of the negative charge within the $\{TiCp^*(NR)(HNR)_2\}^-$ moiety.

In agreement with the observed Ti-N bond distances, Nalewajski-Mrozek[38] bond indices are consistent with single [Ti(1)-N(2) 0.7, Ti(1)-N(3) 0.7] and multiple bonds [Ti(1)-N(1) 1.7]. Small (<0.02) Li-N bond indices were obtained and indicate that these are mostly coulombic interactions; similarly, no evidence of a Ti-Li orbital interaction was identified with this method. While most multiple metal-ligand links have Nalewajski-Mrozek bond indices smaller than the idealized Mülliken orders due to the strongly polar character of the bond, the Ti(1)-N(1) index is rather small. The elongated shape of LMO 155 suggests that the Li^+ ion strongly polarizes the electron density of the Ti-N$_{imido}$ bond. In order to further probe the interatomic interactions, the spatial distribution of electron pairs was examined by calculating the Electron Localization Function (ELF).[39] Figure 5 displays contour plots of the ELF calculated on two planes that are relevant to the Ti(1)-N(1) bond. These ELF cross-sections denote a significant deviation from the idealized cylindrical distribution of electron lone pairs. Such distortion clearly cause by the polarizing ability of the alkali cation.

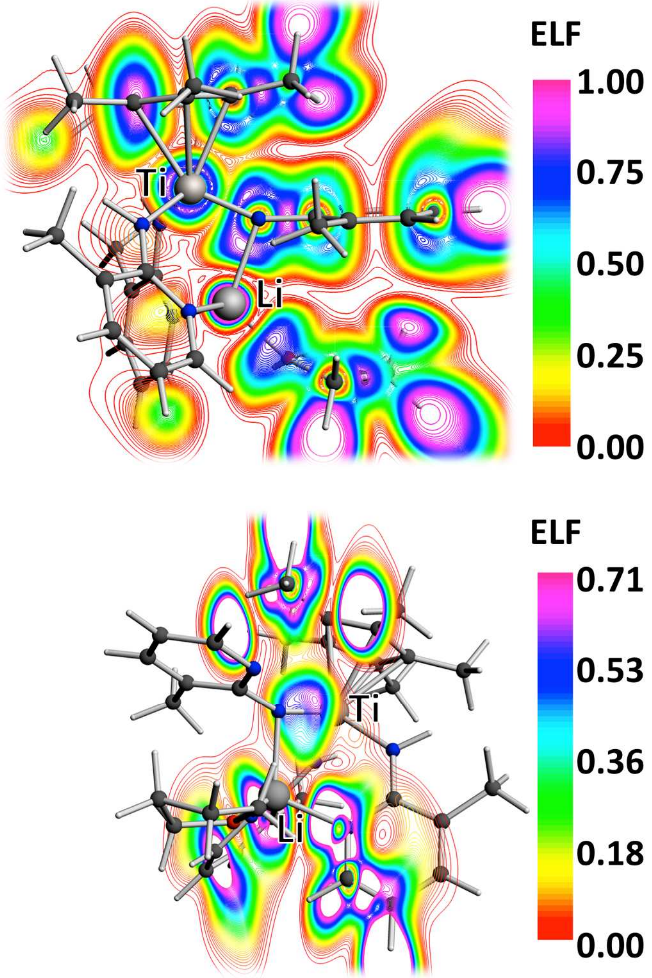


Figure 5. ELF contour maps for **2a**. Top: in the Ti(1)-Li(1)-C(13) plane; bottom: in a plane perpendicular to the Ti(1)-N(1) axis and intersecting the middle point between these atoms.

In summary, the DFT-D calculations confirmed that the Ti-N$_{imido}$ link has a multiple bond character but because of its polarity and the coulombic effect of the Li cation, it is more akin to a double bond. While there is no Ti(1)-Li(1) bonding interaction in **2a,** the electrostatically effect of the alkali metal ion may still impact the reactivity of the Ti-N$_{imido}$ bond.

Conclusions

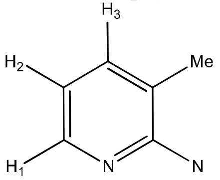
The formation of novel heterometallic titanium imido-pyridine species was achieved by the reaction of LiHNR and [$TiCl_3(\eta^5-C_5Me_5)$]. Depending on stochiometry and reaction temperature the isolation of bridging or terminal imido species was accomplished. When the reaction was performed with a 2:1

stoichiometry, the generation of the dinuclear species $[TiClCp^*(\mu\text{-}NR)]_2$ (**1**) with bridging imido ligands took place. However using an excess of LiNHR, 4:1, the preferential reaction path led to the substitution of all the chloro ligands generating the heterometallic species $[\{Li(THF)\}\{[Ti(\eta^5\text{-}C_5Me_5)(NR)(NHR)_2\}]$ (**2**). In these reactions the isolation of LiCl solvated with amine molecules confirms the dual role of the LiNHR reagents as the source of amido ligands and deprotonating agents. In compounds **1** and **2**, the presence of a pyridine group in the amido or imido ligand has a clear influence in the final structure observed and the pyridinic nitrogen is coordinated to a metal. Compound **2a** is an unusual heterometallic amido-imido derivative with uncommon structural parameters for the imido ligand. DFT calculations for **2a** supported a Ti-N_{imido} double bond character and the electrostatic polarizing effect of the alkali cation on the electron density of the Ti-N_{imido} bond. These calculations also confirmed that there is no Ti-Li bonding interaction and the latter metal ion is bound only by electrostatic interactions. Further studies on the reactivity of these imido compounds in small molecules activation and their behaviour as catalysts precursors in olefin polymerization processes are ongoing.

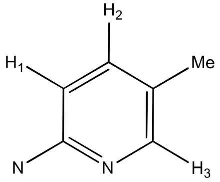
Experimental Section

General Considerations. All manipulations were conducted under an inert atmosphere using Schlenck techniques or in a glove box. All solvents were rigorously dehydrated prior to use. All reagents were used as received from Sigma-Aldrich; with exception of the titanium precursor $[TiCl_3(\eta^5\text{-}C_5Me_5)]$, which was prepared following a reported method.[40] Solution NMR spectra were recorded at 400.13 (^1H), and 100.60 (^{13}C) MHz on a Bruker AV400 spectrometer using CD_2Cl_2 or $CDCl_3$ as solvents. ^1H and ^{13}C chemical shifts are given relative to TMS (δ = 0 ppm) and were measured from the solvent resonances. Elemental analyses were obtained on a Perkin-Elmer Series II 2400 CHNS/O analyser.

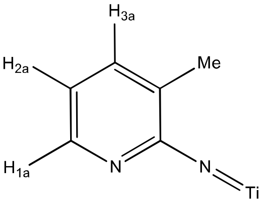
Synthesis of $[TiCl(\eta^5\text{-}C_5Me_5)(\mu\text{-}NR)]_2$ (1a) (NR = 2-imido-3-picoline). 2-amino-3-picoline (0.16 g, 1.32 mmol) was dissolved in 15 mL of dry THF. The mixture was cooled down in a dry ice-acetone bath and ^nBuLi (0.86 mL, 1.32 mmol, 1.6 M) was slowly added. After stirring for 10 minutes, the mixture was allowed to reach room temperature. The solution was cooled down again and $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ (0.20 g, 0.69 mmol), dissolved in 10 mL of dry THF, was added to produce a dark red solution. After stirring for 10 minutes, the mixture was allowed to reach room temperature. The reaction mixture was stirred for two days. Then the solution was concentrated by evaporation under vacuum. After 3 days at 5ºC, compound **1a** was isolated as a dark red solid. *Yield:* 0.07 g, 37%. E.A. calculated for $C_{32}H_{42}Cl_2N_4Ti_2\cdot C_4H_8O$: C, 59.93; H, 6.98; N, 7.76. Found: C, 60.14; H, 7.08; N, 7.42. ^1H NMR (CD_2Cl_2, 20ºC, δ ppm): 7.91 (d, $^3J_{HH}$ = 5 Hz, 2H, H_1), 7.50 (d, $^3J_{HH}$ = 7 Hz, 2H, H_3), 6.83 (dd, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 5 Hz, 2H, H_2), 2.13 (s, 6H, Me), 1.93 (sa, 30H, CH_3-Cp*).

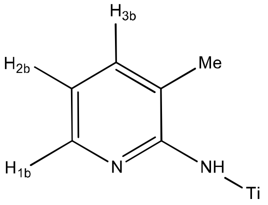


Synthesis of $[TiCl(\eta^5\text{-}C_5Me_5)(\mu\text{-}NR)]_2$ (1b) (NR =2-imido-5-picoline). In a dry Schlenck flask, the 2-amino-5-picoline (0.16 g, 1.32 mmol) was dissolved in 15 mL of dry THF. The mixture was cooled down in a dry ice-acetone bath and ^nBuLi (0.86 mL, 1.32 mmol, 1.6 M) was added. After stirring for 10 minutes, the mixture was allowed to reach room temperature. The mixture was cooled down again and a solution of $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ (0.20 g, 0.69 mmol) in 10 mL of dry THF was added. The resulting dark solution was stirred for 10 minutes and allowed to reach room temperature overnight with stirring. The volume was reduced to a half by evaporation at reduced pressure. Dark red crystals of **1b** were formed at -20ºC in the course of 5 days. *Yield:* 0.096 g, 43%. E.A. calculated for $C_{32}H_{42}Cl_2N_4Ti_2$: C, 59.19; H, 6.52; N, 8.63. Found: C, 58.95; H, 6.32; N, 8.39 ^1H NMR (CD_2Cl_2, 20ºC, δ ppm):7.85 (sa, 2H, H_3), 7.36 (d, $^3J_{HH}$ = 8 Hz, 2H, H_1), 6.24 (d, $^3J_{HH}$ = 8 Hz, 2H, H_2), 2.13 (s, 6H, CH_3), 1.98 (sa, 30H, CH_3-Cp*).

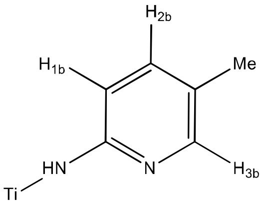


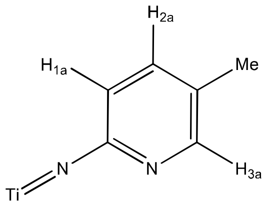
Synthesis of $[\{Li(THF)\}\{[Ti(\eta^5\text{-}C_5Me_5)(NR)(NHR)_2\}]$ (2a) (NR = 2-imido-3-picoline). 2-amino-3-picoline (0.47g, 4.16 mmol) was dissolved in 15 mL of THF and the solution was cooled down in a dry ice-acetone bath (-78ºC). An equimolecular amount of ^nBuLi (1.6 mL, 4.16 mmol, 2.5 M in hexanes) was added. After stirring for 10 minutes, the mixture was allowed to reach room temperature and was stirred for 2 additional hours. To this solution, $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ (0.30 g, 1.04 mmol) dissolved in 10 mL of dry THF, was added. The mixture was heated under reflux during 3 hours. The dark solution was concentrated to half of the volume by evaporation at reduced pressure and stored at 5ºC. After 3 days, orange crystals of **2a** were isolated by filtration, the mother solution was concentrated under vacuum and stored at -20 ºC. After 4 additional days, yellow crystals of $\{[Li(\mu\text{-}Cl)]_2\cdot(NH_2R)_2(THF)_2\}\cdot\{[Li(\mu\text{-}Cl)]_2\cdot(THF)_4\}$ (**3a**) were isolated. Data for **2a**: *Yield:* 0.23 g, 38%. E.A. calculated for $C_{32}H_{43}LiON_6Ti$: C, 65.98; H, 7.44; N, 14.43. Found: C, 65.46; H, 7.31; N, 14.21 ^1H NMR ($CDCl_3$, 20ºC, δ ppm): 7.77 (d,$^3J_{HH}$ = 6 Hz, 1H, H_{1a}), 7.71 (d, $^3J_{HH}$ =5 Hz, 2H, H_{1b}), 7.14 (d, $^3J_{HH}$ = 8 Hz, 1H, H_{3a}), 7.08, (d, $^3J_{HH}$ = 7 Hz, 2H, H_{3b}), 6.42 (dd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, 1H, H_{2a}), 6.29 (dd, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 5 Hz, 2H, H_{2b}), 4.39 (sa, 2H, NH), 3.72 (m, 4H, THF), 2.12 (s, 15H + 9H, Me), 1.81 (m, 4H, THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20ºC, δ ppm): 165.7, (s, C_b, Ar); 156.6, (s, C_a, Ar); 144.9, (s, C_b, Ar); 143.2, (s, C_a, Ar); 137.0, (s, C_b, Ar); 136.3, (s, C_a, Ar); 126.3, (s, C_b, Ar); 124.6, (s, C_a, Ar); 117.7, (s, Csp^2, Cp*); 113.5, (s, C_b); 110.3, (s, C_a); 67.3, (s, THF); 24.9, (s, THF); 11.9 (s, Me, Cp*); 18.4, (s, Me_b); 16.5, (s, Me_a)





Synthesis of [{Li(THF)}{[Ti(η^{5-}C$_5$Me$_5$)(NR)(NHR)$_2$}] (2b) (NR =2-imido-5-picoline). In a procedure similar to the preparation of **2a**, 2-amino-5-picoline (0.47g, 4.16 mmol) was dissolved in 15 mL of THF. The mixture was cooled down to -78ºC and an equimolecular amount of ^{n}BuLi (1.6 mL, 4.16 mmol, 2.5 M in hexanes) was added. After stirring for 10 minutes, the mixture was allowed to reach room temperature and was stirred for 2 hours. To this solution, [Ti(η^5-C$_5$Me$_5$)Cl$_3$] (0.30 g, 1.04 mmol) dissolved in 10 mL of dry THF, was added. The mixture was refluxed for 3 hours. The dark solution produced this way was concentrated to half of the volume by evaporation at reduced pressure and stored at 5ºC. Compound **2b** was isolated as a light red solid by filtration, the mother liquor was concentrated under vacuum and stored at -20 ºC. Yellow crystals of {[Li(μ-Cl)]$_2$·(NH$_2$R)$_3$ (THF)} (**3b**) grew after several days. Data for **2b**: *Yield:* 0.19 g, 32%. E.A. calculated for $C_{32}H_{43}LiON_6Ti$: C, 65.98; H, 7.44; N, 14.43. Found: C, 65.32; H, 7.25; N, 14.16. NMR-^{1}H (CDCl$_3$, 20ºC, δ ppm): 7.71 (sa, 1H, H$_{3a}$), 7.62 (sa, 2H, H$_{3b}$), 7.12 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 ,1H, H$_{1a}$), 6.98 (dd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2, 2H, H$_{1b}$), 6.41 (d, $^3J_{HH}$ = 8 Hz, 1H, H$_{2a}$), 6.10 (d, $^3J_{HH}$ = 8 Hz, 2H, H$_{2b}$), 4.25 (sa, 2H, NH), 3.71 (m, 4H, THF), 1.83 (m, 4H, THF), 2.12 (s, 15H, Cp*), 2.04 (s, 9H, Me). NMR ^{13}C{^{1}H} (CDCl$_3$, 20ºC, δ): 166.5,(s, C$_b$, Ar); 156.9,(s, C$_a$, Ar); 148.3, (s, C$_b$, Ar); 146.2,(s, C$_a$, Ar); 139.3,(s, C$_b$, Ar); 138.8, (s, C$_a$, Ar); 123.5, (s, C$_b$, Ar); 122.5, (s, C$_a$, Ar); 112.5, (s, C$_b$, Ar); 109.0, (s, C$_a$, Ar); 68.6, (s, THF); 26.3, (s, THF); 118.5 (s, Csp^2, Cp*); 12.2, (s,Me, Cp*); 18.1,(s, Me$_b$); 18.0,(s, Me$_a$).





Single-Crystal X-ray Structure Determination of 1b, 2a, 3a and 3b. Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 1. Data collection was performed on a crystal bound to a glass fibre using an inert perfluorinated ether oil and mounted in a stream of cold (200(2) K) nitrogen, in a Bruker-Nonius Kappa CCD single-crystal diffractometer equipped with a graphite-monochromator for Mo-Kα radiation (λ = 0.71073 Å), and an Oxford Cryostream 700 unit. The structures were solved, using the WINGX package,[41] by direct methods (SHELXS-97), completed by the subsequent difference Fourier Techniques and refined by using full-matrix least-squares against F^2 (SHELXL-97).[42] All non-hydrogen atoms were anisotropically refined. Most of the hydrogen atoms were geometrically placed and left riding on their parent atoms, and other were found in the Fourier difference maps.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1056534 [**1b**], CCDC-1056535 [**2a**], CCDC-1056536 [**3a**] and CCDC-1056537 [**3b**].

Table 1. Crystallographic Data for **1b**, **2a, 3a** and **3b.**

	1b	**2a**	**3a**	**3b**
Formula	$C_{32}H_{42}Cl_2N_4Ti_2$	$C_{32}H_{43}LiN_6OTi$	$C_{18}H_{32}Cl_2Li_2N_2O_3$	$C_{22}H_{32}Cl_2Li_2N$
FW	649.40	582.56	409.24	481.32
Cryst size (mm^3)	0.21-0.23-0.20	0.44-0.34-0.15	0.30-0.20-0.20	0.41-0.33-0.20
Color	Dark Red	Orange	Colourless	Colourless
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*c*
a/ Å	9.570(2)	11.414(8	8.7259(8)	10.457(11)
b/ Å	16.1114(13)	15.790(9)	18.065(2)	28.056(8)
c/ Å	10.626(3)	18.041(7)	15.231(2)	9.083(7)
α (°)	90	90	90	90
β (°)	111.075(17)	90	101.634(9)	100.46(8)
γ (°)	90	106.06(4)	90	90
V/ Å^3	1528.8(8)	3125(3)	2351.6(5)	2621(3)
Z	2	4	4	4
ρ_{calcd}, g cm^{-3}	1.411	1.234	1.156	1.220
μ, mm^{-1}	0.726	0.308	0.293	0.272
F(000)	680	1240	872	1016
θ range (deg)	3.26 - 27.50	3.43 - 25.56	3.18 - 27.50	3.10 -25.57
θ comp. [%]	99.3	99.5	99.5	99.4
Reflns collected	10644	19158	41232	37790
R(int)	0.1192	0.100	0.1556	0.1527
Data/restraints/params	3490/0/181	5822/0/402	5380/30/252	4882/0/390
GOF	1.119	1.086	1.095	1.104
R$_1$, wR$_2$ [I > 2σ (I)] ^{a}	0.0695/ 0.1309	0.0844/ 0.1560	0.0750/ 0.1965	0.0685/ 0.1516
R$_1$, wR$_2$ [all data] ^{a}	0.1532/ 0.1643	0.1334/ 0.1793	0.1013/ 0.2235	0.1152/ 0.1797
Diff peak / hole (e Å^{-3})	0.584/-0.552	1.078/-0.896	0.536/-0.458	0.386/-0.596

^{a} $R_1 = \sum||F_0|-|F_c||/[\sum|F_0|]$; $wR_2 = \{[\sum w(F_0^2 - F_c)^2] / [\sum w(F_0^2)^2]\}^{1/2}$

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Notes and references

[a] Departamento de Química Orgánica y Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain. pilar.gomez@uah.es, martaeg.mosquera@uah.es.

[b] Department of Chemistry and Chemical Biology, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada, L8S 4MI

[c] Present address: Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, United States.

† Electronic Supplementary Information (ESI) available: [X-ray crystallographic data in CIF format.]. See DOI: 10.1039/b000000x/

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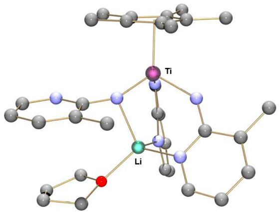
Imido-Pyridine Ti(IV) Compounds: Synthesis of Unusual Imido-Amido Heterobimetallic Derivatives.

S. Pedrosa,[a] F. Vidal,[a,c] L. Myongwon Lee,[b] I. Vargas-Baca,[b] P. Gómez-Sal[a,]* and M. E. G. Mosquera [a,]*



Controlled generation of novel bridging or terminal imido-pyridine complexes is achieved, including the unusual species $[Li(THF)][Ti(\eta^5\text{-}C_5Me_5)(NR)(NHR)_2]$. Computational studies corroborate its charge-separated nature.