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Reversible double insertion of aryl isocyanates into the Ti–O bond of titanium(IV) isopropoxide

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Abstract

The insertion of phenyl isocyanate into titanium isopropoxide leads to the formation of a dimeric complex $[Ti(O^iPr)_2(\mu\text{-}O^iPr)\{C_6H_5N(O^iPr)CO\}]_2$ (**1**) which has been structurally characterized. Reaction of titanium isopropoxide with two and more than 2 equiv. of phenyl isocyanate is complicated by competitive, reversible insertion between the titanium carbamate and titanium isopropoxide. The ligand formed by insertion of phenyl isocyanate into the titanium carbamate has been structurally characterized in its protonated form $C_6H_5N\{C(O^iPr)O\}C(O)N(H)C_6H_5$ (**3aH**). Insertion into the carbamate is kinetically favored whereas insertion into isopropoxide gives the thermodynamically favored product.

Keywords: Aryl isocyanates; Multiple insertion; Titanium isopropoxide; Reversible insertion

1. Introduction

Homogeneous catalytic processes often involve insertion of neutral substrates into transition metal-X bonds as one of the key steps, where X is carbon, oxygen, or nitrogen [1]. In the metal promoted polymerization of olefins for example, multiple insertion of the olefin into the metal alkyl group is the key step in the propagation of the polymer chain [2]. Consequently, mechanistic studies involving the insertion of a M–X group into a neutral substrate are of great importance in unraveling factors that promote or deter multiple insertion [3]. Recently the elegant work of Jordan and coworkers [4] involving the multiple insertion of chloro alkenes has brought to light complications involved in polymerization. A good understanding of this key reaction would permit one to control this reaction and enable design of catalysts for polymerization of new substrates. Similarly, incorporation of neutral polar substrates like CO_2, CS_2, isocyanates, and isothiocyanates, into polymers could be of great value in synthesizing functionalized polymers [5]. While insertions of polar heterocumulenes into M–N [6], M–C [7] and M–O [8] have been studied with a variety of metals, especially with titanium [9,10], and zirconium [11], multiple insertions of heterocumulenes have not been studied extensively [12,13]. Well characterized reactions involving multiple insertions are mainly those of alkynes [12a,14], nitriles [15], isocyanides [16], and carbon monoxide [17]. Apart from these instances, only a few examples of alkenes that stop at double insertions [18] are known. Notably, structurally characterized products from titanium alkoxide insertion into heterocumulenes are very few [19].

In this study we show how insertion reactions of aryl isocyanates follow complex pathways due to opposing electronic and steric requirements. In the presence of isopropoxide and carbamate, insertion of aryl isocyanate into carbamate is kinetically favored over direct insertion into isopropoxide. This results in a product

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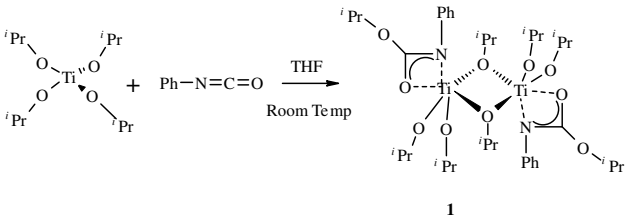
that has undergone double insertion of aryl isocyanate and is thermodynamically uphill. The product of double insertion slowly reverts to give the carbamate (the mono insertion product).

2. Results and discussion

2.1. Insertion of phenyl isocyanate

Mehrotra and coworkers [9b] had shown by ebullioscopic measurements that treatment of titanium isopropoxide with 1 equiv. of an isocyanate leads to the formation of a dimeric complex. However, Meth-Cohn et al. [10]. had recorded the ^{1}H NMR of the reaction of titanium isopropoxide with 1 equiv. of phenyl isocyanate (Eq. (1)) in carbon tetrachloride. They could distinguish only two methine protons contrary to what is expected for **1**.



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(1)

We recorded ^{1}H NMR of this reaction mixture in $CDCl_3$ and found three septets at 4.49, 4.76 and 5.10 ppm. We assign these to the methine proton of isopropoxide which is either terminal, bridged, or on the carbamate (obtained by the insertion of phenyl isocyanate into the titanium isopropoxide), respectively. The distinctive resonances in $CDCl_3$ are consistent with the dimeric structure and permit us to follow the reaction much better. The assignments of the resonances are based on the preferential hydrolysis of the carbamate in complex **1**.

When a solution of complex **1** in petroleum ether was cooled to −20 °C, single crystals suitable for X-ray analysis were obtained (Fig. 1). A crystallographic investigation was taken up to confirm the nuclearity and bonding modes proposed for the complex. The molecular structure of compound **1** is centro-symmetric. (Crystallographic parameters are given in Table 1.) The most interesting feature of this molecule is the chelating nature of the carbamate. (Selected bond lengths and bond angles are given in Table 2.) The asymmetric unit contains only one half of the complete structure, containing two terminal isopropoxides, one bridging isopropoxide and one carbamate. Both titanium atoms are six coordinate. The terminal isopropoxides are at a distance of 1.77 Å from the titanium. The bridging isopropoxides are not equidistant from both titanium atoms, the distances are 1.93 and 2.11 Å. The carbamate is chelated

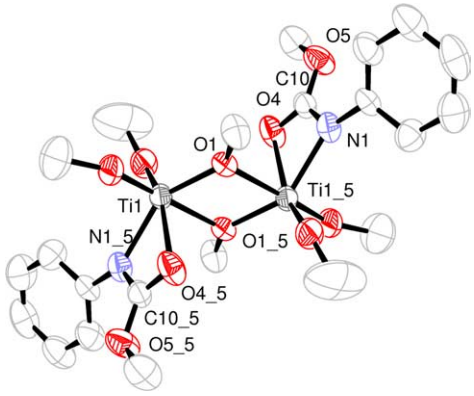


Fig. 1. Structure of compound **1**. Methyl groups on the isopropyl moiety have been omitted for clarity.

with the Ti–N distance being 2.11 Å and Ti–O distance 2.24 Å. The N–C–O angle was found to be 115.6° and the C–Ti–N angle was found to be 60.2°. The C–N and the C–O distance of the NCO unit was intermediate between a single and a double bond at 1.33 and 1.25 Å, respectively, due to delocalization of the double bond. The plane of the phenyl ring was found to be 36° with respect to the plane containing the Ti–N–C–O. In an analogous reaction of carbon dioxide, it was recently found that the carbonate prefers a bridging mode [20]. Carboxylate groups also prefer to have a bridging mode [21]. The higher symmetry in solution required by ^{1}H NMR spectrum is presumably due to fluxional behavior.

Addition of a second equivalent of phenyl isocyanate led to the formation of a complex (Eq. (2)) which had four sets of methine resonances: one at 5.10 ppm, two sets between 4.88 and 4.70 ppm and one at 4.49 ppm in the ratio 3.6:3:3. The peaks at 5.10 and 4.49 ppm are assigned to the isopropoxide on the carbamate in a chelated fashion and the terminal isopropoxide on the titanium in accordance with what had been observed for complex **1**. In the presence of trace quantities of moisture, ^{1}H NMR of the reaction mixture also showed a peak at 5.01 ppm due to partial hydrolysis. The complex ^{1}H NMR pattern observed is not consistent with a simple structure proposed for **2**. As this complex could not be crystallized by cooling or precipitation for carrying out further characterization, it was decomposed by addition of water. On deliberate hydrolysis, ^{1}H NMR of the solution showed two sets of methine resonances at 5.01 and at 4.00 ppm assigned to the isopropyl group of the carbamic acid ester and isopropanol in the ratio 1:1. This shows that the reaction mixture indeed has two isocyanates inserted into two of the isopropoxides on the titanium.

On the basis of the new peaks in ^{1}H NMR in the range 4.85–4.70 ppm, it is unlikely that the proposed complex **2** has a static structure as shown in Eq. (2).

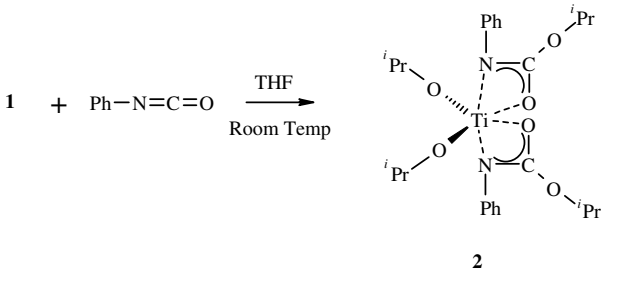
Table 1
Crystallographic data for compound **1** and **3aH**

Compound	**1**	**3aH**
Empirical formula	$C_{19}H_{33}NO_5Ti$	$C_{17}H_{18}N_2O_3$
Formula weight	403.36	298.33
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pccn*	*Pbca*
Unit cell dimensions		
a (Å)	18.521(4)	8.894(4)
b (Å)	23.791(7)	16.300(7)
c (Å)	10.340(5)	22.681(10)
Volume (Å^3)	4556(3)	3288(3)
Z	8	8
Color and shape	Colorless, hexagonal	Colorless, needle
Absorption coefficient (mm^{-1})	0.401	0.084
F(000)	1728	1264
Diffractometer	Enraf Nonius CAD4	SMART CCD Area Detector
Crystal size (mm^3)	$0.40 \times 0.39 \times 0.38$	$0.44 \times 0.18 \times 0.06$
Theta range for data collection (°)	1.39–24.98	1.80–26.06
Reflections collected	4003	24,130
Independent reflections (R_{int})	4003 (0.0000)	3231 (0.1060)
Completeness to theta	24.98° = 100.0%	26.06° = 99.7%
Absorption correction	Empirical (DIFABS)	Empirical
Max. and min. transmission	0.923 and 0.4824	0.995 and 0.961
Data/restraints/parameters	4003/0/235	3231/0/271
Goodness-of-fit on F^2	1.050	1.012
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0794$, $wR_2 = 0.2078$	$R_1 = 0.0599$, $wR_2 = 0.1317$
R indices (all data)	$R_1 = 0.1882$, $wR_2 = 0.3109$	$R_1 = 0.1142$, $wR_2 = 0.1554$
Largest diff. peak and hole (e/Å^3)	0.456 and −0.480	0.130 and −0.119

Table 2
Bond lengths and bond angles for compound **1**

Ti(1)–O(1)	1.934(4)	O(1)–Ti(1)–O(1)#1	74.0(2)
Ti(1)–O(1)#1	2.112(4)	O(1)–Ti(1)–N(1)#1	145.6(2)
Ti(1)–N(1)#1	2.116(6)	O(1)#1–Ti(1)–N(1)#1	87.2(2)
Ti(1)–O(4)#1	2.236(5)	O(1)–Ti(1)–O(4)#1	89.00(19)
Ti(1)–Ti(1)#1	3.233(2)	O(1)#1–Ti(1)–O(4)#1	84.33(18)
O(4)–C(10)	1.258(8)	N(1)#1–Ti(1)–O(4)#1	60.1(2)
O(5)–C(10)	1.303(8)	Ti(1)–O(1)–Ti(1)#1	106.0(2)
N(1)–C(10)	1.328(8)	C(10)–N(1)–Ti(1)#1	94.1(4)

The new peaks present in the proposed complex **2**, which were not present in complex **1**, were reduced in intensity on lowering the temperature.



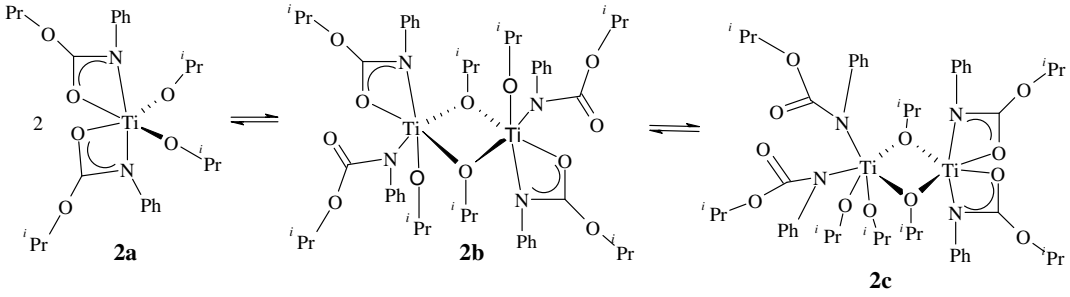
2 (2)

To aid structural assignment, variable temperature NMR of **2** was attempted. At temperatures below −20 °C, the two sets of peaks at 4.85–4.70 ppm separate out and also the relative intensities of these peaks decrease. The bridged isopropoxide appears at 4.76 ppm, as in complex **1**. Ratios of the peaks in the three regions keep changing and at −40 °C it was found to be 2:1:2. Concomitant gain in the peaks corresponding to the chelated species is observed. This process was found to be reversible and on returning to room temperature, the ratio of the peaks in the three regions was found to be 3.6:3:3 again.

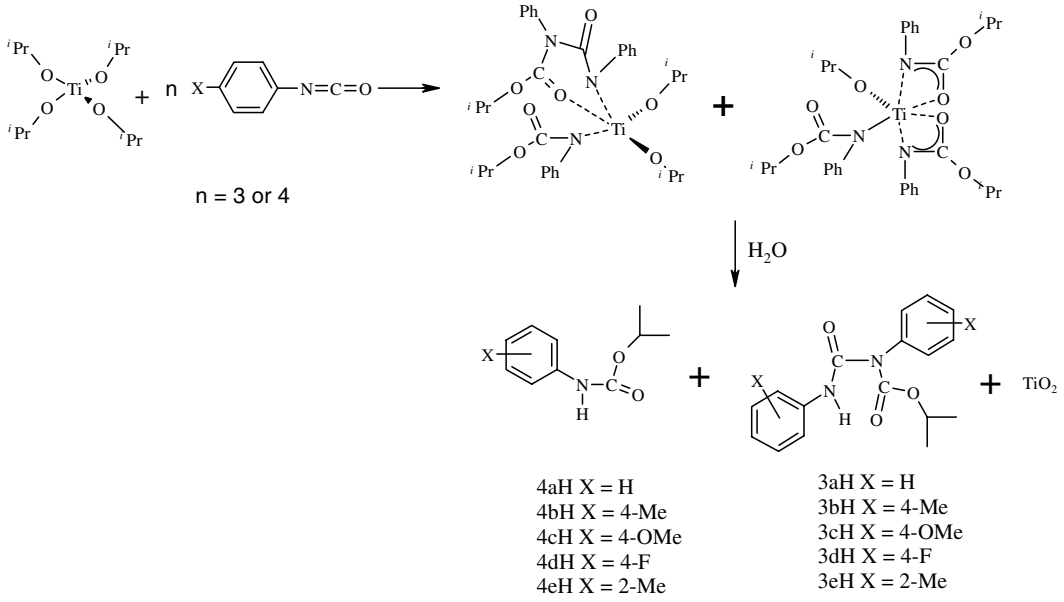
The proposed complex **2** may be in dynamic equilibrium with other complexes as shown in Scheme 1.

2.2. Multiple insertions

Titanium has two isopropoxides on the proposed complex **2** that are still capable of undergoing further insertion reactions. The reaction mixture obtained on treatment of titanium isopropoxide with 3 equiv. of phenyl isocyanate was analyzed by ^{1}H NMR. It showed three sets of methine resonances at 5.10, 5.01 and 4.76 ppm in the ratio of 3:6:4 whereas the reaction mixture from the reaction of 4 equiv. of phenyl isocyanate had the same sets in the ratio 2:7:2. The peak at 5.10 ppm is for the chelated carbamate and the peak at 4.76 ppm is a mixture of the bridged isopropoxide and the monodentate carbamate based on assignments made for the proposed complex **2**. The peak at 5.01 ppm is



Scheme 1. Hypothetical solution-structures of dinuclear alkoxide-bridged species in equilibrium with the proposed compound **2**.



Scheme 2. Double insertion of aryl isocyanate and the organic products isolated.

obtained by the superimposition of septets resulting from the protonated carbamate (**4aH**) and the compound obtained upon insertion of the phenyl isocyanate into the titanium carbamate resulting in the formation of the ligand $\{C_6H_5N^-C(O)N(C_6H_5)C(O)O^iPr\}$ bound to the titanium through the nitrogen. These assignments were supported by the hydrolysis studies on these reaction mixtures. The complexes were hydrolyzed (Scheme 2) and ^1H NMR of the organic products showed peaks at 10.9 ppm, in addition to those expected for the carbamic acid and isopropanol.

Fortuitously, the organic product having the unusually low field peak at 10.9 ppm, crystallized out. X-ray analysis showed it to be the product **3aH** (Fig. 2), formed by the insertion of a second phenyl isocyanate into the carbamate. Multiple insertion of alkyl isocyanate into isopropoxide had been suggested by Meth-Cohn et al. [10] as a product formed in the presence of a large excess of the isocyanate. Crystallographic characterization also revealed the cause of the low field resonance, the hydrogen on the nitrogen (H2) is intramolecularly hydrogen bonded to O2 in compound **3aH** and resonates at 10.9 ppm (selected bond lengths and bond angles are given in Table 3).

The double insertion of aryl isocyanate into isopropoxide leading to the formation of coordinated **3a**

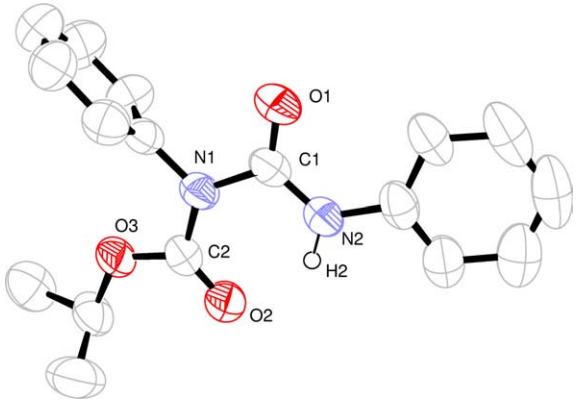


Fig. 2. Molecular structure of compound **3aH**. Hydrogen atoms on carbon have been omitted for clarity.

Table 3
Bond lengths and bond angles for compound **3aH**

O(1)–C(1)	1.210(3)	C(2)–N(1)–C(1)	125.79(19)
O(2)–C(2)	1.203(2)	O(1)–C(1)–N(2)	125.0(2)
O(3)–C(2)	1.329(3)	O(1)–C(1)–N(1)	118.2(2)
N(1)–C(2)	1.385(3)	N(2)–C(1)–N(1)	116.8(2)
N(1)–C(1)	1.421(3)	O(2)–C(2)–O(3)	124.8(2)
N(2)–C(1)	1.342(3)	O(2)–C(2)–N(1)	125.0(2)
N(2)–H(2)	0.88(3)	O(3)–C(2)–N(1)	110.2(2)
H(2)···O(2)	1.98(2)	N(2)–H(2)···O(2)	133.9(19)

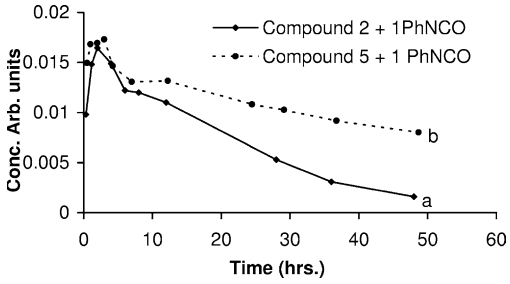


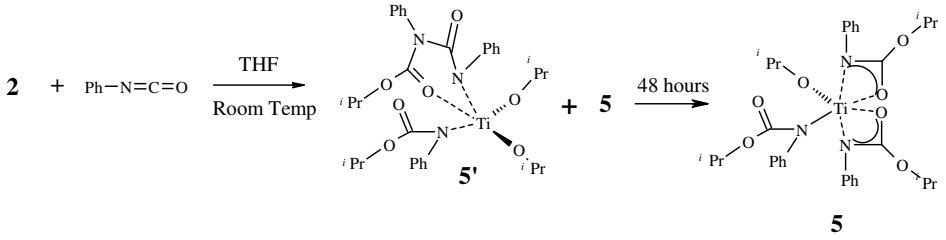
Fig. 3. Concentration of **3aH** as a function of time on addition of PhNCO to (a) **2** → **5** and (b) **5** → **6**.

suggests a competitive insertion of phenyl isocyanate between the titanium-isopropoxide and titanium-carbamate (**4a**) (Scheme 2).

We then checked to see if the concentration ratios of coordinated **3a** and **4a** are invariant as a function of time. The reaction of compound **2** with 1 equiv. of phenyl isocyanate (Eq. (3)) led to the formation of a mixture of products (**5** and **5′**). Concentration of coordinated **3a** and **4a** was followed by hydrolysis with stoichiometric quantities of water and ^{1}H NMR analysis. The concentration of **3aH** reached a maximum and then showed a steady decay (graph a, Fig. 3), whereas the concentration of **4aH** increased with time. Ultimately the complex had only 3 equiv. of **4a** and 1 equiv. of isopropoxide coordinated to titanium after a period of about 48 h. This suggests that coordinated **3a** has transferred one phenyl isocyanate molecule into isopropoxide to form a molecule with three coordinated **4a** ligands.

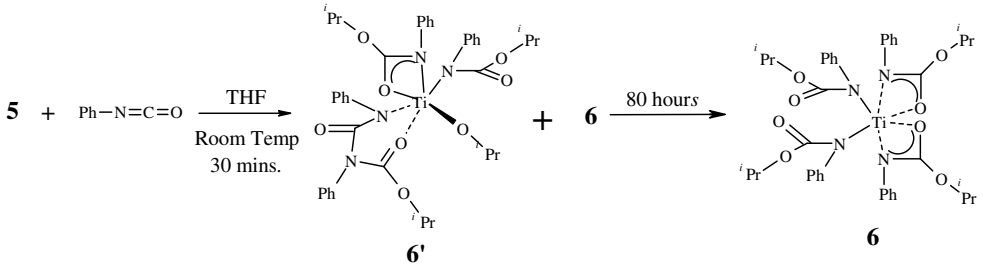
These concentration profiles show that the multiple insertion is a reversible process and not an irreversible competitive reaction to give **5** and **5′**. In fact formation of **5**, having coordinated **4a**, probably follows two different pathways (Scheme 3). One of them involves a reversible insertion of the incoming isocyanate into the Ti–N bond in preference to the Ti–O bond (process A) to give **5′**. This complex then gets converted into a complex having two coordinated **4a** ligands (proposed compound **5**) by an intramolecular rearrangement (process B). The alternative competing pathway (process C), is a reversible double insertion followed by a direct insertion to give a complex containing three coordinated **4a** ligands (proposed compound **5**).

The concentration profiles of **4aH** showed a jump upon addition of 1 equiv. of the phenyl isocyanate to either **2** or **5**. This jump corresponded to 57% of the added isocyanate in the case of **2** and 38% in the case of **5**. Pathway A is competing with C favorably although it leads to a less stable compound **5′** (proposed). Subse-



(3)

A similar formation and decay of **3aH** (graph b, Fig. 3) was observed when the proposed complex **5** containing three coordinated **4a** ligands and one isopropoxide was treated with 1 equiv. of the isocyanate (Eq. (4)).



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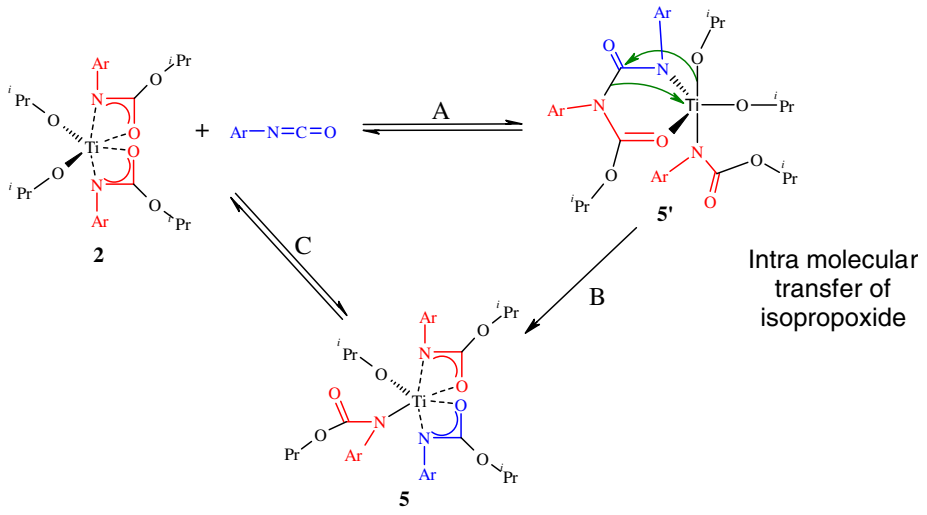


Scheme 3. Proposed intramolecular and reversible reinsertion pathway for the conversion of the double insertion product to the mono insertion product.

quently the conversion of coordinated **3a** into coordinated **4a** can take place either through pathways C or B. The conversion of **2**:**5** and subsequently to **6** were also studied with the 4-fluorophenyl isocyanate and similar concentration changes were observed.

The double insertion is favored by kinetic factors arising from the comparable nucleophilicity of the coordinated nitrogen in comparison with the coordinated oxygen. This proposal concurs with a few reports in the literature where the preference for insertion of isocyanate into M–N bonds over insertions into M–O bonds [22,23] has been reported. These studies had been conducted with coordinated OR and NR_2 (where R is an alkyl group). It is interesting that in the present system, even an NAr (Ar = aryl) group attached to a COOR is nucleophilic enough to compete with an OR (R = alkyl) group. Subsequently, thermodynamic factors convert the intermediate to form the more stable **5**. Thus coordinated **4a** ligand functions as a molecular ferry, to transfer the phenyl isocyanate to an isopropoxide.

The conversion of **5**′ to **5**, where the coordinated **3a** and isopropoxide is transformed to two **4a** ligands, is probably driven by the steric differences between the two ligands. This steric demand of **3a** can be visualized by modeling studies based on the structure of complex **1**. The structure of a simulated complex is shown in Fig. 4 using the coordinates of **3aH** in the program WEBLAB® VIEWER [24]. Coordinated **4a** has a cone angle of 104°, whereas coordinated **3a** is estimated to have a cone angle of 171° based on the crystal structure of **3aH**. A cone angle of 64° for the isopropoxide ligand is estimated in the structure of complex **1**. The steric congestion is relieved by conversion of coordinated **3a** with an isopropoxide into two **4a** ligands (Fig. 4).

To verify the reversibility of mono and double insertion an experiment similar to the classical crossover

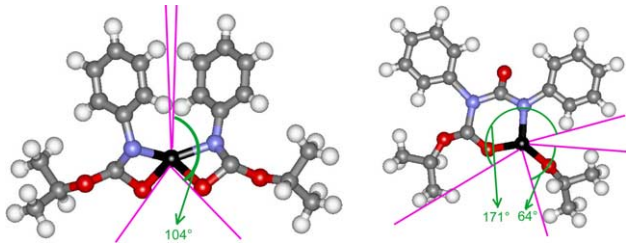
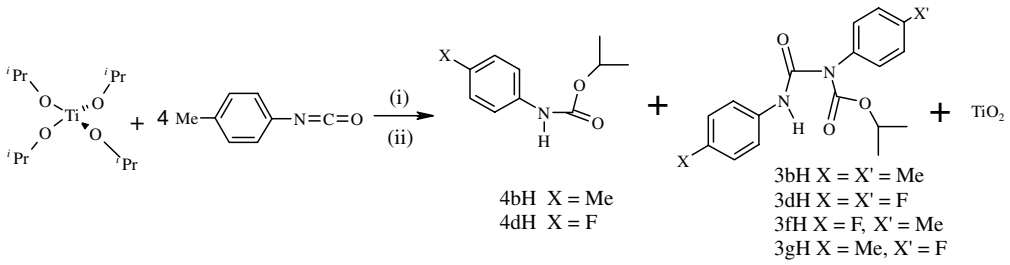


Fig. 4. Steric requirements of two mono inserted ligands versus a double inserted ligand and isopropoxide.

experiment was conducted (Scheme 4). The reaction of titanium isopropoxide was carried out with 4 equiv. of 4-methylphenyl isocyanate. Conversion of **3b**:**4b** was confirmed by ^{1}H NMR and took 108 h. A ^{1}H NMR spectrum of the organic fraction after deliberate hydrolysis of an aliquot of the reaction mixture showed the ratio of **4bH** to free isopropanol to be 7.4:1 and the ratio of **3bH**:**4bH** was 1:52. Concentration of **3bH** was obtained from NMR analysis of the peak at 10.9 ppm. At this stage 2 equiv. of 4-fluorophenyl isocyanate was added to the reaction mixture. The reaction was monitored with time and showed the formation of the mixed double insertion product **3f**. As time progressed, formation of **3d** and even **3g** coordinated to titanium, was inferred from analysis of the hydrolysis products. Compound **3gH** can only be formed if a second insertion of 4-methylphenyl isocyanate was carried out on **4d**. This reaction was monitored for 60 h. After which the ratios of **4bH**, **4dH** and **3**(**b**,**d**,**f**,**g**)*H* formed on hydrolysis with water were estimated by ^{1}H NMR and gas chromatography and are discussed below.

It was found that the reaction mixture contained **3** and **4** in the ratio 1:18. The products from the double insertion of the aryl isocyanate (**3dH**, **3fH**, **3bH** and



Scheme 4. A pseudo crossover experiment to find out the reversibility of mono and double insertion. (i) After 108 h, 2 eq. 4-fluorophenyl isocyanate was added and stirred for 60 h. (ii) Organic fraction extracted after hydrolysis with water.

3gH) were present in the ratio 1:0.9:1.6:1.2. The ratio of **4bH** and **4dH** was estimated by gas chromatography and was found to be in the ratio 1:0.61. This shows that the insertion of aryl isocyanate both into Ti–O^{i}Pr bond and into the coordinated carbamate is completely reversible. Electron withdrawing substituents in the *para* position of the isocyanate appear to have favored the insertion leading to a bias in the ratio of **4bH** and **4dH**. Further exploration of the electronic requirements in the reaction follow.

2.3. Electronic effects on the formation of *3* and *4*

A competition experiment was carried out with a mixture of 4-methoxyphenyl isocyanate, 4-fluorophenyl isocyanate and titanium isopropoxide in a 1:1:1 ratio at 193 K. It was found that after 10 min., the ratio of **4dH**:**4cH** was 72:28 which became 64:36 after 30 min and 1:1 after 1 h. The insertion reaction is clearly faster with 4-fluorophenyl isocyanate than with 4-methoxyphenyl isocyanate. A similar competition experiment between 4-methoxyphenyl isocyanate and 4-methylphenyl isocyanate and titanium isopropoxide was carried out by mixing them in the ratio 1:1:1 at 193 K. After 10 min the ratio of **4cH**:**4bH** was found to be 64:36, which slowly equilibrates to 1:1 ratio in 1 h showing that the insertion is faster with 4-methoxyphenyl isocyanate compared to 4-methylphenyl isocyanate. This implies that only the inductive effect of the 4-methoxy group is operational. If a resonance effect is in operation, then it would have behaved as an electron-donating group and its rate would have been slower. This contrasts with the reactions between aryl isocyanates and 2-ethylhexanol where a resonance effect is operative [25]. The present result implies that the aryl isocyanate binds to titanium with the lone pair prior to insertion, so that the resonance effect is not operative.

2.4. Steric effects on the formation of *3* and *4*

Surprisingly the steric demands of **3** and **4** do not vary with substituents on the aromatic group in a simple fashion. Steric requirements of **3e** are about the same as **3b** whereas **4e** requires significantly greater space than **4b** (as simulated by WebLab Viewer shown in the supporting information). This has interesting consequences on the ratio of **3e**:**4e** as a function of time. When titanium isopropoxide was treated with 4 equiv. of 2-methylphenyl isocyanate, the ratio of **3eH**:**4eH** in the organic fraction reached 1:1.5 against 1:3.4 in the reaction with 4-methylphenyl isocyanate. Over time, the ratio of **3eH**:**4eH** only fell to about 1:3.7 in 60 h. Whereas in the reaction of 4-methylphenyl isocyanate, the ratio **3bH**:**4bH** became 1:9.5 in the same time period. There was no further drop in the concentration of **3eH**, whereas the **3bH**:**4bH** ratio fell to 1:47 in 108 h. This experiment shows how the conversion from **3** to **4** is an equilibrium process controlled by steric requirements. Conversion from coordinated **3** to coordinated **4** does not provide as much steric relief in the case of 2-methylphenyl isocyanate as in the case of 4-methylphenyl isocyanate.

3. Conclusion

We have shown that the insertion of a second molecule of heterocumulene into a Ti–O^{i}Pr bond, takes place by two different paths. The coordinated carbamate picks up the free isocyanate and transfers it to a coordinated isopropoxide. The comparable nucleophilicity of the coordinated nitrogen makes insertion of aryl isocyanate into the carbamate facile. The ligand formed from double insertion of aryl isocyanate readily converts to two coordinated carbamates if an isopropoxide is present.

The insertion reactions are favored by the polarization of the heterocumulene to form a positive charge on the carbon. Thus the reaction is favored by electron withdrawing groups on the *para* position of the isocyanates. The electron withdrawing effect is through induction.

The presence of an *ortho*-substituted arene prevents the complete conversion of the coordinated double inserted product to the coordinated carbamate. Significant amounts of the double inserted product remain at the end of the reaction. Thus the second step is primarily driven by steric requirements.

4. Experimental

4.1. General

All manipulations were carried out under an inert atmosphere of dry nitrogen using a standard double manifold. Tetrahydrofuran and petroleum ether were freshly distilled from sodium/benzophenone prior to use. Titanium tetraisopropoxide, phenyl isocyanate, 4-methoxyphenyl isocyanate, 4-fluorophenylisocyanate, 2-methylphenyl isocyanate were obtained from Aldrich and 4-methylphenyl isocyanate was obtained from Lancaster and used as supplied.

4.2. Physical measurements

^{1}H NMR and ^{13}C{^{1}H} spectra were recorded either on a Bruker ACF 200 MHz, Bruker AMX400 or on a Bruker Avance 400 operating at 200 MHz for ^{1}H NMR and 50 MHz for ^{13}C NMR (Bruker ACF 200 MHz) and at 400 and 100 MHz, respectively, for the 400 MHz. spectrometers, with tetramethylsilane (TMS) as the internal reference. All spectra were recorded in $CDCl_3$ as the solvent. For compounds **3aH**, **4aH** and **4bH**, representative coupled ^{13}C NMR were recorded as additional evidence for identifying the compounds. NMR spectra could only be obtained for a mixture of **5** and **6** as no separation could be accomplished. HRESMS was recorded on a Micromass Q-Tof micro instrument (Electrospray ionization, ESI). Elemental analyses were carried out on a Carlo Erba elemental analyzer model 1106. GC measurements were made using a Chemito GC 7610 instrument with a flame ionization detector and a packed column (0.32 mm i.d., 2.44 m length) having 5% SE-30 as the liquid phase and Ch-W(HP) as the solid phase. Nitrogen was used as a carrier gas at a flow rate of 30 cm^3/min. A temperature program (1 min at 100 °C ramp to 120 °C at 10 °C/min then ramp to 250 °C at 25 °C/min and hold at 250 °C for 2 min) run was employed with the injector being maintained at 200 °C and the detector at 260 °C, to analyze the organic products in the crossover experiments.

4.3. X-ray crystallography

The single crystal of complex **1** were highly sensitive to air and decomposed even in the mother liquor, hence the crystal were taken out in paraffin oil for mounting. A good quality crystal of complex **1** was chosen and mounted in a Lindemann capillary with paraffin oil and a crystal of compound **3aH** was glued to the tip of a glass fiber along the largest dimension for indexing and data collection. Data for complex **1** was collected on an Enraf-Nonius CAD4 single crystal diffractometer equipped with graphite-monochromatized Mo Kα radiation, whereas data for compound **3aH** was collected on a Bruker AXS single crystal diffractometer equipped with SMART APEX CCD detector and a sealed Mo Kα source working at 1.75 kW. Intensity data were collected at 293(2) K. For complex **1**, accurate unit cell parameters and orientation matrices were determined by least-squares refinement of 25 well-centered reflections in the range $9° \leqslant \theta \leqslant 13°$. Three periodically measured reference reflections showed no significant decay during the time of data collection. For compound **3aH** the SMART software was used for data acquisition and the SAINT software for data extraction. The data were corrected for Lorentz and polarization effects. Absorption correction for complex **1** was done with DIFABS [26] and for compound **3aH** SADABS [27] was used for the absorption correction. All computations were performed using the WINGX package [28]. The positions of heavy atoms were determined by SHELXS-86 [29]. The remaining atoms were located from the difference Fourier map using SHELXL-97 [30]. For complex **1** the H-atoms were geometrically fixed with the respective non H-atoms and allowed to ride.

4.4. Synthesis of compound *1*

Titanium tetraisopropoxide (1 ml, 3.38 mmol) was dissolved in 20 ml of tetrahydrofuran and into this solution, phenyl isocyanate (0.37 ml, 3.38 mmol) was added. The mixture was stirred for 8 h and the solvent evaporated to dryness under vacuum. The residue was washed with 2–3 ml of cold petroleum ether. The remaining white solid was redissolved in 25 ml of warm petroleum ether which on slow cooling resulted in the formation of colorless crystals (950 mg, 70%). These crystals were highly sensitive to moisture and decomposed immediately on exposure to air. ^{1}H NMR (200 MHz) δ 7.28–7.22 (m, 8H), 7.04–7.00 (m, 2H), 5.10 (sept, 2H, J = 6.2 Hz), 4.76 (sept, 2H, J = 6.2 Hz), 4.49 (sept, 4H, J = 6.2 Hz), 1.31 (d, 12H, J = 6.2 Hz), 1.25 (d, 24H, J = 6.2 Hz), 1.12 (d, 12H, J = 6.2 Hz). ^{13}C NMR (100 MHz) 154.1 {N*C*=O(O^{i}Pr)}, 139.4 (Ph), 129.1 (Ph), 123.1 (Ph), 119.1 (Ph), 68.5 (terminal O^{i}Pr*C*H), 68.1 (bridged O^{i}Pr*C*H), 64.3 (inserted O^{i}Pr*C*H), 25.9 (terminal O^{i}Pr*C*H$_3$), 25.5 (bridged O^{i}Pr*C*H$_3$), 22.3 (inserted O^{i}Pr*C*H$_3$).

4.5. Reaction of titanium isopropoxide with 2 equiv. of phenyl isocyanate

Titanium tetraisopropoxide (1 ml, 3.38 mmol) was dissolved in 20 ml of tetrahydrofuran. Into this solution, phenyl isocyanate (0.74 ml, 6.76 mmol) was added. The

mixture was stirred for 9 h and the solvent evaporated to dryness under vacuum to give a dark orange paste. This residue was extracted with minimum quantity of petroleum ether and dried under vacuum to give a red orange paste. This gave a mixture of complexes **2** (800 mg, 45%). ^{1}H NMR (200 MHz) δ 7.41–7.27 (m, 32H), 7.12–6.97 (m, 16H), 5.11 (OC*H* sept, 3.6H, $J = 6.2$ Hz), 4.76 (OC*H* sept, 3H, $J = 6.2$ Hz), 4.49 (OC*H* sept, 3H, $J = 6.2$ Hz), 1.31 (CHCH_3 d, 22H, $J = 6.2$ Hz), 1.26 (CHCH_3 d, 18H, $J = 6.2$ Hz), 1.17 (CHCH_3 d, 18H, $J = 6.2$ Hz). On attempting to crystallize out the pure compound, hexagonal crystal of complex **1** were formed.

4.6. Compound *3aH*

Carbamic acid, phenyl[(phenylamino) carbonyl]-, 1-methylethyl ester: titanium tetraisopropoxide (1 ml, 3.38 mmol) was dissolved in 20 ml of tetrahydrofuran. After addition of phenyl isocyanate (1.48 ml, 13.52 mmol), the mixture was stirred for 3 h, and the solvent evaporated to dryness under vacuum to give an orange red paste. This mixture was redissolved in methylene chloride and taken in a separating funnel washed with distilled water and the organic part extracted. This organic mixture contains both **4aH** and **3aH** in the ratio 7:3. They were separated by running a preparative TLC with 1% ethyl acetate in petroleum ether (total yield 80%). ^{1}H NMR (400 MHz) δ 10.88 (s, 1H, NH), 7.47 (d, 2H, $J = 7.6$ Hz), 7.31 (m, 3H), 7.22 (t, 2H, $J = 7.6$ Hz), 7.11 (d, 2H, $J = 7.6$ Hz), 6.99 (t, 1H, $J = 7.6$ Hz), 4.91 (OC*H* sept, 1H, $J = 6.2$ Hz), 1.07 (CHCH_3 d, 6H, $J = 6.2$ Hz). ^{13}C NMR (100 MHz) δ 155.6 {PhN*C*=O(O^{i}Pr)}, 151.6 {PhN*C*=O(NPh)}, 137.8 (*ipso* t, $^2J_{CH} = 9.5$ Hz), 137.2 (*ipso* t, $^2J_{CH} = 9.5$ Hz), 128.9 (Ph dd, $^1J_{CH} = 156.9$ Hz, $^2J_{CH} = 3.3$ Hz), 128.8 (Ph dd, $^1J_{CH} = 159.9$ Hz, $^2J_{CH} = 8.0$ Hz), 128.7 (Ph dd, $^1J_{CH} = 159.2$ Hz, $^2J_{CH} = 7.7$ Hz), 128.0 (Ph dt, $^1J_{CH} = 161.0$ Hz, $^2J_{CH} = 7.3$ Hz), 123.8 (Ph dt, $^1J_{CH} = 157.7$ Hz, $^2J_{CH} = 8.8$ Hz), 119.8 (Ph d, $^1J_{CH} = 162.5$ Hz), 71.7 (O*C*H d sept, $^1J_{CH} = 149.7$ Hz, $^2J_{CH} = 4.0$ Hz), 21.5 (CH*C*H$_3$ dd, $^1J_{CH} = 126.9$ Hz, $^2J_{CH} = 4.3$ Hz). Anal. Calc. for $C_{17}H_{18}N_2O_3C$, 68.43; H, 6.08; N, 9.39. Found: C, 68.09; H, 6.23; N, 9.17%.

4.7. Compound *4aH*

Carbamic acid, phenyl-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 7.42 (d, 2H, $J = 7.6$ Hz), 7.29 (t, 2H, $J = 7.6$ Hz), 7.05 (t, 1H, $J = 7.6$ Hz), 6.92 (s, NH), 5.05 (OC*H* sept, 1H, $J = 6.2$ Hz), 1.30 (CHCH_3 d, 6H, $J = 6.2$ Hz) ^{13}C NMR (100 MHz) δ 153.7 {PhN*C*=O(O^{i}Pr)}, 138.4 (*ipso*), 129.0 (Ph dd, $^1J_{CH} = 161.0$ Hz, $^2J_{CH} = 9.2$ Hz), 123.2 (Ph dt, $^1J_{CH} = 159.4$ Hz, $^2J_{CH} = 8.4$ Hz), 119.0 (Ph d, $^1J_{CH} = 166.3$ Hz), 68.7 (O*C*H d, $^1J_{CH} = 150.3$ Hz), 22.1 (CH*C*H$_3$ qd, $^1J_{CH} = 126.6$ Hz, $^2J_{CH} = 4.6$ Hz). Anal. Calc. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.81. Found: C, 66.92; H, 7.33; N, 7.55%.

4.8. Compound *4bH*

Carbamic acid, (4-methylphenyl)-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 7.28 (d, 2H, $J = 8.0$ Hz), 7.08 (d, 2H, $J = 8.0$ Hz), 6.84 (s, NH), 5.02 (OC*H* sept, 1H, $J = 6.2$ Hz), 2.29 (PhCH_3 s, 3H) 1.28 (CHCH_3 d, 6H, $J = 6.2$ Hz) ^{13}C NMR (100 MHz) δ 153.6 {PhN*C*=O(O^{i}Pr)}, 135.7 (*ipso*), 132.7 (*ipso*-*C*CH$_3$ m, $^2J_{CH} = 5.9$ Hz), 129.5 (Ph ddm, $^1J_{CH} = 156.0$ Hz, $^2J_{CH} = 5.1$ Hz $^3J_{CH} = 6.8$ Hz), 119.0 (Ph d, $^1J_{CH} = 160.2$ Hz), 68.5 (O*C*H d, $^1J_{CH} = 150.0$ Hz), 22.1 (CH*C*H$_3$ qd, $^1J_{CH} = 126.3$ Hz, $^2J_{CH} = 5.1$ Hz), 20.7 (Ph*C*H$_3$qt, $^1J_{CH} = 126.3$ Hz, $^2J_{CH}$=4.2 Hz). Anal. Calc. for $C_{11}H_{15}NO_2$ C, 68.37; H, 7.82; N, 7.24. Found: C, 68.64; H, 7.91; N, 6.86%.

4.9. Compound *4cH*

Carbamic acid, (4-methoxyphenyl)-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 7.27 (d, 2H, $J = 8.8$ Hz), 6.84 (d, 2H, $J = 8.8$ Hz), 6.41 (s, NH), 4.99 (OC*H* sept, 1H, $J = 6.4$ Hz), 3.77 (OCH_3 s, 3H), 1.28 (CHCH_3 d, 6H, $J = 6.4$ Hz) ^{13}C NMR (100 MHz) δ 155.6 (*ipso*-*C*OCH$_3$), 153.7 {PhN*C*=O(O^{i}Pr)}, 131.2 (*ipso*), 120.5 (Ph), 114.0 (Ph), 68.3 (O*C*H), 55.3 (O*C*H$_3$), 22.0 (CH*C*H$_3$). Anal. Calc. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.22; N, 6.69. Found: C, 63.47; H, 7.20; N, 6.13%.

4.10. Compound *4dH*

Carbamic acid, (4-fluorophenyl)-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 7.33 (dd, 2H, $J = 9.4$ Hz, $^4J_{HF} = 4.8$ Hz), 6.99 (dd, 2H, $J = 9.4$ Hz, $^3J_{HF} = 8.4$ Hz), 6.50 (s, NH), 5.01 (OC*H* sept, 1H, $J = 6.6$ Hz), 1.28 (CHCH_3 d, 6H, $J = 6.6$ Hz) ^{13}C NMR (100 MHz) δ 158.8 (*ipso*-*C*F d, $^1J_{CF} = 241.0$ Hz), 153.4 {PhN*C*=O(O^{i}Pr)}, 134.1 (Ph d, $^4J_{CF} = 2.0$ Hz), 120.34 (Ph br), 115.5 (Ph d, $^2J_{CF} = 22.7$ Hz), 68.8 (O*C*H), 22.0 (CH*C*H$_3$). HRESMS $(M + Na)^+$ obsd. *m*/*z* 220.0751. Anal. Calc. for $C_{10}H_{12}FNO_2Na$: 220.0749.

4.11. Compound *4eH*

Carbamic acid, (2-methylphenyl)-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 7.83 (d, 1H, br), 7.21 (t, 1H, $J = 7.8$ Hz), 7.16 (d, 1H, $J = 7.8$ Hz), 7.01 (t, 1H, $J = 7.8$ Hz), 6.34 (NH), 5.03 (OC*H* sept, 1H, $J = 6.4$ Hz), 2.26 (PhCH_3 s, 3H), 1.31 (CHCH_3 d, 6H, $J = 6.4$ Hz). ^{13}C NMR (100 MHz) δ 153.3 {PhN*C*=O(O^{i}Pr)}, 135.7 (*ipso*), 129.9 (*ipso*-*C*CH$_3$), 127.7 (Ph), 126.2 (Ph), 123.6 (Ph), 121.1 (Ph), 68.1 (O*C*H), 21.6 (CH*C*H$_3$), 17.2 (Ph*C*H$_3$). HRESMS $(M + Na)^+$ obsd. *m*/*z* 216.0999, calc. for $C_{11}H_{15}NO_2Na$: 216.1000.

4.12. Compound **3bH**

Carbamic acid, 4-methylphenyl[(4-methylphenylamino)carbonyl]-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 10.86 (s, 1H, NH), 7.42 (d, 2H, J = 8.0 Hz), 7.19 (d, 2H, J = 8.0 Hz), 7.09 (d, 2H, J = 8.0 Hz), 7.05 (d, 2H, J = 8.0 Hz), 5.01 (OC*H* sept, 1H, J = 6.2 Hz), 2.37 (PhCH_3 s, 3H), 2.29 (PhCH_3 s, 3H), 1.16 (CHCH_3 d, 6H, J = 6.2 Hz). ^{13}C NMR (100 MHz) δ 155.6 {PhN*C*=O(O^{i}Pr)}, 151.6 {PhN*C*=O(NPh)}, 137.6 (*ipso*), 135.2 (*ipso*), 134.4 (*ipso*-*C*CH$_3$), 133.1 (*ipso*-*C*CH$_3$), 129.2 (Ph), 129.2 (Ph), 128.2 (Ph), 119.7 (Ph), 71.4 (O*C*H), 21.3 (CH*C*H$_3$), 20.9 (Ph*C*H$_3$), 20.6 (Ph*C*H$_3$). HRESMS (M + H)$^+$ obsd. *m*/*z* 327.1734, calc. for $C_{19}H_{23}N_2O_3$: 327.1709.

4.13. Compound **3cH**

Carbamic acid, 4-methoxyphenyl[(4-methoxyphenylamino)carbonyl]-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 10.78 (s, 1H, NH), 7.45 (d, 2H, J = 8.8 Hz), 7.09 (d, 2H, J = 8.8 Hz), 6.91 (d, 2H, J = 8.8 Hz), 6.83 (d, 2H, J = 8.8 Hz), 4.98 (OC*H* sept, 1H, J = 6.4 Hz), 3.83 (OCH_3 s, 3H), 3.77 (OCH_3 s, 3H), 1.16 (CHCH_3 d, 6H, J = 6.4 Hz). ^{13}C NMR (100 MHz) δ 158.9(ipso*C*OCH$_3$), 156.1 (*ipso*-*C*OCH$_3$), 155.9 {PhN*C*=O(O^{i}Pr)}, 152.0 {PhN*C*=O(NPh)}, 133.5 (*ipso*), 131.1 (*ipso*), 130.0 (Ph), 129.6 (Ph), 121.5 (Ph), 114.1 (Ph), 71.5 (O*C*H), 55.5 (O*C*H$_3$), 55.4 (O*C*H$_3$), 21.6 (CH*C*H$_3$). HRESMS (M + Na)$^+$ obsd. *m*/*z* 381.1434, calc. for $C_{19}H_{22}N_2O_5Na$: 381.1426.

4.14. Compound **3dH**

Carbamic acid, 4-fluorophenyl[(4-fluorophenylamino)carbonyl]-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 10.92 (s, 1H, NH), 7.48 (dd, 2H, J = 9.4 Hz, $^4J_{HF}$ = 4.7 Hz), 7.16 (dd, 2H, J = 9.4 Hz, $^4J_{HF}$ = 4.7 Hz), 7.07 (dd, 2H, J = 9.4 Hz, $^3J_{HF}$ = 8.2 Hz), 6.94 (dd, 2H, J = 9.4 Hz, $^3J_{HF}$ = 8.2 Hz), 5.00 (OC*H* sept, 1H, J = 6.2 Hz), 1.16 (CHCH_3 d, 6H, J = 6.2 Hz). ^{13}C NMR (100 MHz) δ 161.9 (*ipso*-*C*F d, $^1J_{CF}$ = 244.0 Hz), 159.1 (*ipso*-*C*F d, $^1J_{CF}$ = 244.0 Hz), 155.4 {PhN*C*=O(O^{i}Pr)}, 151.8 {PhN*C*=O(NPh)}, 133.6 (*ipso*, d, $^4J_{CF}$ = 3.0 Hz), 132.9 (*ipso* d, $^4J_{CF}$ = 3.0 Hz), 130.3 (Ph d, $^3J_{CF}$ = 8.0 Hz), 121.6 (Ph d, $^3J_{CF}$ = 8.0 Hz), 115.4 (Ph d, $^2J_{CF}$ = 23.0 Hz), 115.3 (Ph d, $^2J_{CF}$ = 23.0 Hz), 72.0 (O*C*H), 21.3 (CH*C*H$_3$). HRESMS (M + Na)$^+$ obsd. *m*/*z* 357.1038, calc. for $C_{17}H_{16}F_2N_2O_3$Na: 357.1027.

4.15. Compound **3eH**

Carbamic acid, 2-methylphenyl[(2-methylphenylamino)carbonyl]-, 1-methylethyl ester: ^{1}H NMR (400 MHz) δ 10.98 (NH), 8.08 (d, 1H, J = 7.8 Hz), 7.27 (d, 1H, J = 7.8 Hz), 7.21 (m, 4H), 7.16 (d, 1H, J = 7.8 Hz), 7.03 (t, 1H, J = 7.8 Hz), 5.04 (OC*H* sept, 1H, J = 6.4 Hz), 2.40 (PhCH_3 s, 3H), 2.21 (PhCH_3 s, 3H), 1.18 (CHCH_3 d, 3H, J = 6.4 Hz), 1.16 (CHCH_3 d, 3H, J = 6.4 Hz). ^{13}C NMR (100 MHz) δ 155.3 {PhNC=O(O^{i}Pr)}, 150.9 {PhNC=O(NPh)}, 136.2 (*ipso*), 136.1 (*ipso*), 135.6 (*ipso*-*C*CH$_3$), 130.2 (*ipso*-*C*CH$_3$), 129.9 (Ph), 128.4 (Ph), 128.1 (Ph), 127.3 (Ph), 126.3 (Ph), 123.7 (Ph), 120.7 (Ph), 120.6 (Ph), 71.1 (O*C*H), 21.2 (CH*C*H$_3$), 17.9 (Ph*C*H$_3$), 17.0 (Ph*C*H$_3$). HRESMS (M + Na)$^+$ obsd. *m*/*z* 349.1534, calc. for $C_{19}H_{22}N_2O_3$Na: 349.1528.

4.16. Reaction of titanium isopropoxide with 3 equiv. of phenyl isocyanate

Titanium tetraisopropoxide (1 ml, 3.38 mmol) was dissolved in 20 ml of tetrahydrofuran. Into this solution, phenyl isocyanate (1.1 ml, 10.1 mmol) was added. The mixture was stirred for 54 h and the solvent evaporated to dryness under vacuum resulting in an orange–red paste (1.42 g, 68%). This reaction mixture was found to be mostly the proposed compound **5** with trace quantities of the complex with coordinated **3a**. ^{1}H NMR (400 MHz) δ 7.55–6.86 (m, 65H), 5.10 (OC*H* sept, 3H, J = 6.2 Hz), 5.01 (OC*H* sept, 6H, J = 6.2 Hz), 4.80 (OC*H* sept, 4H, J = 6.2 Hz), 1.31 (CHCH_3 d, 54H, J = 6.2 Hz), 1.19 (CHCH_3 d, 24H, J = 6.2 Hz).

4.17. Reaction of titanium isopropoxide with 4 equiv. of phenyl isocyanate

Titanium tetraisopropoxide (1 ml, 3.38 mmol) was dissolved in 20 ml of tetrahydrofuran. Into this solution, phenyl isocyanate (1.48 ml, 13.52 mmol) was added. The mixture was stirred for 80 h and the solvent evaporated to dryness under vacuum resulting in an orange–red paste (1.72 g, 65%). This reaction mixture was found to be the proposed compound **6** with a trace quantity of the complex containing coordinated **3a**. ^{1}H NMR (400 MHz) δ 7.55–6.86 (m, 55H), 5.1 (OC*H* sept, 2H, J = 6.2 Hz), 5.01 (OC*H* sept, 7H, J = 6.2 Hz), 4.80 (OC*H* sept, 2H, J = 6.2 Hz), 1.31 (CHCH_3 d, 54H, J = 6.2 Hz), 1.19 (CHCH_3 d, 12H, J = 6.2 Hz).

4.18. General procedure followed to carry out the kinetic measurements

Titanium tetraisopropoxide (0.25 ml, 0.845 mmol.) was dissolved in 30 ml of tetrahydrofuran. Into this solution aryl isocyanate (3.38 mmol) was added. The mixture was stirred at room temperature and the reaction was monitored at regular intervals by withdrawing aliquots of 0.2 ml. The complex was decomposed by addition of water and ^{1}H NMR of the organic fraction was recorded. Concentrations of the organic ligands **4H**

and **3H** were estimated from the integrals of the corresponding methine and NH protons.

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Appendix A. Supplementary data

Cone angles of *ortho*-substituted ligands are marked on a simulated molecular structure diagram. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 251819 for compound **1** and CCDC No. 251820 for compound **3aH**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.11.038.

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