



# Room temperature metathesis of aryl isocyanates and aromatic aldehydes catalyzed by group(IV) metal alkoxides: An experimental and computational study

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## ABSTRACT

Aromatic aldehydes and aryl isocyanates do not react at room temperature. However, we have shown for the first time that in the presence of catalytic amounts of group(IV) *n*-butoxide, they undergo metathesis at room temperature to produce imines with the extrusion of carbon dioxide. The mechanism of action has been investigated by a study of stoichiometric reactions. The insertion of aryl isocyanates into the metal *n*-butoxide occurs very rapidly. Reaction of the insertion product with the aldehyde is responsible for the metathesis. Among the *n*-butoxides of group(IV) metals, Ti(O<sup>*n*</sup>Bu)<sub>4</sub> (**8aTi**) was found to be more efficient than Zr(O<sup>*n*</sup>Bu)<sub>4</sub> (**8aZr**) and Hf(O<sup>*n*</sup>Bu)<sub>4</sub> (**8aHf**) in carrying out metathesis. The surprisingly large difference in the metathetic activity of these alkoxides has been probed computationally using model complexes Ti(OMe)<sub>4</sub> (**8bTi**), Zr(OMe)<sub>4</sub> (**8bZr**) and Hf(OMe)<sub>4</sub> (**8bHf**) at the B3LYP/LANL2DZ level of theory. These studies indicate that the insertion product formed by Zr and Hf are extremely stable compared to that formed by Ti. This makes subsequent reaction of Zr and Hf complexes unfavorable.

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## 1. Introduction

Formation of new carbon–carbon bonds by a metal carbene catalyzed olefin metathesis has found wide utility in synthetic chemistry [1]. Stoichiometric and catalytic exchange between multiply bonded substrates has been extended to metathesis of carbon–heteroatom double bonds recently [2,3]. Carbodiimide metathesis is catalyzed by a number of complexes leading to formation of unsymmetrical carbodiimides [4]. Group 14 complexes catalyze metathesis of phenyl isocyanates to give *N,N* diphenyl carbodiimides and carbon dioxide [5]. The reverse reaction, metathesis of carbon dioxide with carbodiimide leading to formation of isocyanates has also been demonstrated [6].

While the metathesis coupling of heterocumulenes are well explored, there are few reports that describe the metathesis of isocyanates and carbonyl compounds leading to imines [7]. These reactions proceed under drastic conditions with poor yields in the absence of catalysts. The yields can be improved by the use of metal carbonyls as catalysts, but they still require high temperatures [8]. Guiducci et al. have reported the use of cyclopentadienyl–amidinate titanium imido compounds for the conversion of carbonyl compounds to imines at elevated temperatures [9a]. Very recently Meyer et al. have shown that mid and high valent uranium amido and imido derivatives promote multiple bond metathesis

with carbon dioxide to give isocyanates and uranium oxo complexes [9b].

Contrary to the high temperature metathesis reported till date, we report here a room temperature metathesis of aromatic aldehydes and aryl isocyanates to give imines and carbon dioxide catalyzed by simple group(IV) metal alkoxides. Theoretical calculations are performed on the model complexes Ti(OMe)<sub>4</sub>, Zr(OMe)<sub>4</sub> and Hf(OMe)<sub>4</sub> at B3LYP/LANL2DZ level of theory to get an insight into these reactions.

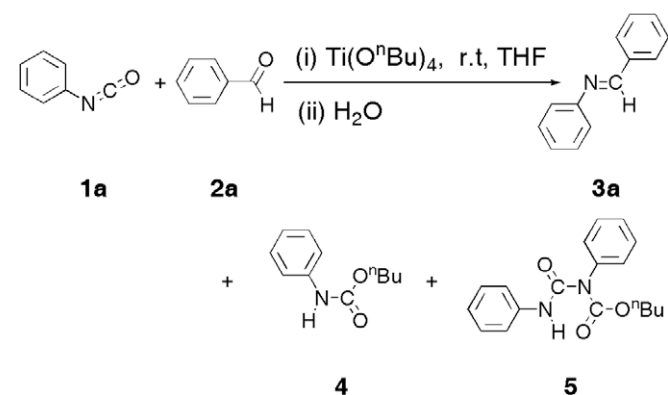
## 2. Results and discussion

### 2.1. Reaction of phenyl isocyanate with benzaldehyde in the presence of Ti(O<sup>*n*</sup>Bu)<sub>4</sub>

The reaction of equivalent amounts of phenyl isocyanate (PhNCO) and benzaldehyde (PhCHO) was initially carried out in the presence of 10 mol% of titanium(IV) *n*-butoxide {Ti(O<sup>*n*</sup>Bu)<sub>4</sub>} at room temperature (Entry 1, Table 1). The reaction was monitored by <sup>1</sup>H NMR and was found to be complete in 60 h. The products were analyzed and found to contain significant amounts of the metathesis product *N*-benzylidene(aniline) **3a**. However the major product, butyl *N*-phenylcarbamate **4**, and trace amounts of butyl 2,4-diphenylallophanate **5**, arose from the insertion of the butoxy group into PhNCO [10]. The amount of imine **3a** formed was found to increase when Ti(O<sup>*n*</sup>Bu)<sub>4</sub> was reduced to a smaller amount (Entry 2, Table 1). Subsequent reactions showed that titanium *n*-

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**Table 1**  
Reaction of phenyl isocyanate with benzaldehyde mediated by  $\text{Ti}(\text{O}^n\text{Bu})_4$ .



Entry	$\text{Ti}(\text{O}^n\text{Bu})_4$ (mol%)	Ratio of products <sup>a</sup> (%)			Yield <sup>b</sup> <b>3a</b> (%)	TON
		<b>3a</b>	<b>4</b>	<b>5</b>		
1	10.0	41	58	1	44	4.4
2	1.0	73	27	–	72	72.0
3	0.1	95	5	–	76	760.0
4	100.0	17	83	–	18	0.2
5	25.0	28	72	–	24	1.0

<sup>a</sup> Ratio of products were determined by  $^1\text{H NMR}$ .

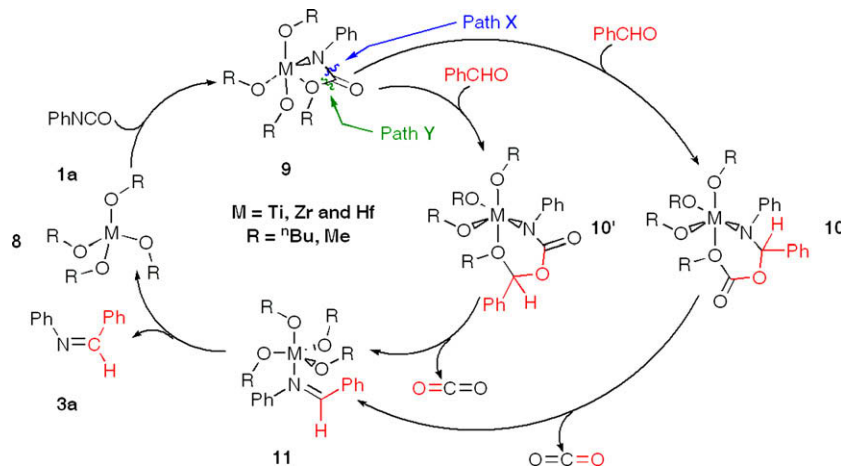
<sup>b</sup> All yields are wt% with respect to aldehyde after 60 h of reaction.

butoxide can be utilized in even smaller quantities to convert isocyanates to imines under ambient conditions (Entry 3, Table 1).

To understand these reactions, we examined the stoichiometric reactions of metal alkoxides with the reactants (Entry 4, Table 1). Metal alkoxides do not react with benzaldehyde. However they undergo very rapid insertion reaction with isocyanates to produce a carbamate ligand coordinated to titanium which has been characterized [10]. A control experiment was carried out to determine whether the carbamate generated from  $\text{Ti}(\text{O}^n\text{Bu})_4$  could carry out the metathesis reaction.  $\text{Ti}(\text{O}^n\text{Bu})_4$  was treated with four equivalents of  $\text{PhNCO}$  and stirred at room temperature. The reaction was followed by  $^1\text{H NMR}$  and when all the  $\text{PhNCO}$  had undergone insertion, four equivalents of benzaldehyde were added. Analysis of the reaction mixture after work up indicated the formation of metathesis product **3a** in 24% yield (Entry 5, Table 1).

## 2.2. Plausible mechanism

Insertion of phenyl isocyanate into the  $\text{M}-\text{OR}$  bond of metal alkoxide **8** would generate a metal carbamate complex **9** (Scheme 1).



**Scheme 1.** Proposed mechanism for the metathesis coupling of isocyanate and aldehyde.

Hydrolysis of complex **9** gives rise to product **4**. The reaction of complex **9** with benzaldehyde can proceed via two paths, either by insertion of aldehyde into the  $\text{C}-\text{N}$  bond (path **X**) or by insertion of aldehyde into the  $\text{C}-\text{O}$  bond (bond between the carbonyl carbon and alkoxy oxygen in the carbamate group) (path **Y**). If initial insertion is followed by insertion of aldehyde into the  $\text{C}-\text{N}$  bond of **9** then it results in complex **10** (path **X**). Complex **10** may then extrude  $\text{CO}_2$  to give **11** which in turn loses the coordinated imine to generate the metal alkoxide **8**. Alternatively, if there is aldehyde insertion into the  $\text{C}-\text{O}$  bond of **9**, then it leads to complex **10'** (path **Y**). This is similar to the second insertion observed with isocyanates at elevated temperatures in a head to head fashion permitting  $\text{CO}_2$  extrusion (Scheme 2) [6e,10].

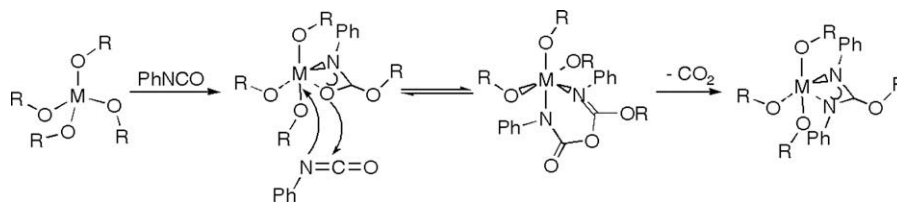
## 2.3. Reaction of aryl isocyanates with aromatic aldehydes with varying electronic demands

The metathesis reaction was carried out with aryl isocyanates and aryl aldehydes having different electronic demands (Table 2). The metathesis reaction was found to proceed most efficiently for a combination of an aryl isocyanate with an electron donating group and an aryl aldehyde with an electron withdrawing group. Based on these results, one might conclude that the insertion of alkoxide into isocyanate is not a rate limiting step. If it was, then electron withdrawing groups on isocyanate would have accelerated the reaction [6e,10]. Insertion of the aldehyde into the  $\text{C}-\text{O}/\text{C}-\text{N}$  bond of **9** must have a higher energy of activation. This explains why electron deficient aldehydes react faster with the electron rich isocyanates which have undergone insertion.

In the reaction of salicylaldehyde with phenyl isocyanate, one would have expected the formation of **6** and **7** (Scheme 3). Product **6** is formed by the nucleophilic addition of hydroxyl group of **3j** to the  $\text{C}=\text{O}$  of isocyanate. Similarly **7** will be the product arising from the nucleophilic addition of hydroxyl group of salicylaldehyde to the  $\text{C}=\text{O}$  of isocyanate. However in the above reaction, both **6** and **7** were absent and **3j** was formed as the only product. This indicates that coupling is faster than nucleophilic addition in this case. Hence the reaction is tolerant to aldehydes with nucleophilic functional groups such as a hydroxyl group.

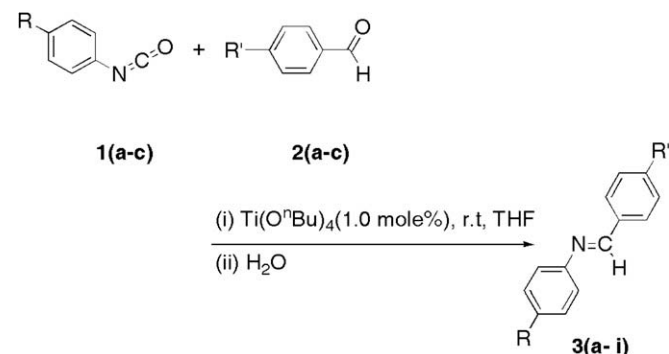
## 2.4. Metathesis reaction catalyzed by group(IV) metal alkoxides

The reaction of *p*-methoxyphenyl isocyanate with *p*-cyanobenzaldehyde was then attempted with various group(IV) metal alkoxides as catalysts (Scheme 4). All these reactions resulted in the formation of imine **3e** and trace amounts (<1%) of carbamate **4**.



**Scheme 2.** Insertion of two molecules of phenyl isocyanate in head to head fashion and elimination of carbon dioxide.

**Table 2**  
Metathesis reaction with substrates of varying electronic demands.



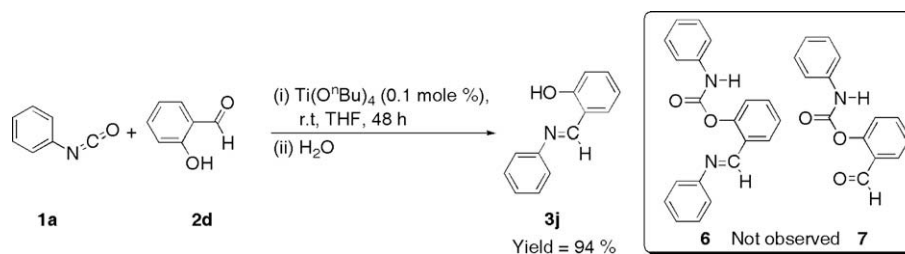
Entry	R	R'	Product	Yield <sup>a</sup> (%)	TON
1	H	H	<b>3a</b>	70	70
2	H	OMe	<b>3b</b>	70	70
3	H	CN	<b>3c</b>	78	78
4	F	CN	<b>3d</b>	70	70
5	OMe	CN	<b>3e</b>	83	83
6	OMe	H	<b>3f</b>	68	68
7	OMe	OMe	<b>3g</b>	70	70
8	F	OMe	<b>3h</b>	61	61
9	F	H	<b>3i</b>	68	68

<sup>a</sup> All yields are wt% with respect to aldehyde after 54 h of reaction.

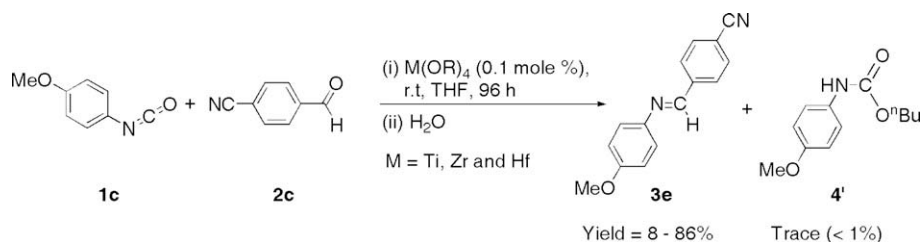
The yield of **3e** with Ti as catalyst was found to be better than Zr and Hf (Table 3). In the case of Zr and Hf significant amounts of unreacted aldehyde was observed in the crude product. The <sup>1</sup>H

NMR spectra of the crude products obtained in the reaction of *p*-methoxyphenyl isocyanate with *p*-cyanobenzaldehyde in the presence of titanium(IV) *n*-butoxide, zirconium(IV) *n*-butoxide and hafnium(IV) *n*-butoxide is given in Fig. 1. The peak at 10.09 ppm corresponds to the C–H of the aldehyde and that at 8.52 ppm is for the C–H of the imine. Comparison of the relative intensities of these two peaks in the products obtained with Ti(O<sup>*n*</sup>Bu)<sub>4</sub>, Zr(O<sup>*n*</sup>Bu)<sub>4</sub> and Hf(O<sup>*n*</sup>Bu)<sub>4</sub> clearly indicates that the metathesis reaction is more favored with Ti than with Zr and Hf. In addition all the spectra show formation of trace amounts of **4'**. A distinct triplet is observed at 0.95 ppm which corresponds to the methyl proton of the butoxy group in the carbamate **4'**. The carbamate **4'** results from hydrolysis of insertion intermediate such as **9**. It is likely that in the case of Zr and Hf, the reaction of **9** with aldehyde to give **10/11** is less favored and hence after the reaction one observes unreacted aldehyde and **4'** which is the hydrolysis product of **9**. Hence one may assume that the formation of **9** quenches the catalyst in case of Zr and Hf. However in the case of Ti, it happens after many cycles.

Further, Zirconium(IV) *n*-butoxide was found to be less efficient than its heavier congener hafnium(IV) *n*-butoxide. The observed reactivity pattern appears to follow the trend in the ionic sizes of these elements. The ionic sizes for the four coordinate Ti, Zr and Hf in their +4 oxidation state are 56, 73 and 72 pm, respectively [11]. Ti being the smallest among the group(IV) elements is found to be the most efficient metathesis catalyst. On the other hand Hf which is slightly smaller than Zr is found to be a better metathesis catalyst than the latter. So it is likely that the five coordinate intermediates **9**, **10** and **11** involved in the metathesis reaction are stabilized to a greater extent for Zr and Hf compared to that of Ti. Between Zr and Hf, these intermediates are more stabilized for Zr compared to Hf owing to the smaller size of Hf.



**Scheme 3.** Reaction of phenyl isocyanate with salicylaldehyde in the presence of 0.1 mol% Ti(O<sup>*n*</sup>Bu)<sub>4</sub>.



**Scheme 4.** Metathesis reaction of *p*-methoxyphenyl isocyanate with *p*-cyanobenzaldehyde mediated by group(IV) metal alkoxides.

**Table 3**

Metathesis reaction of *p*-methoxyphenyl isocyanate with *p*-cyanobenzaldehyde mediated by group(IV) metal alkoxides.

Entry	M(OR) <sub>4</sub>	% Conversion <sup>a</sup>	Yield <sup>b</sup> <b>3e</b> (%)	TON
1	Ti(O <sup><i>n</i></sup> Bu) <sub>4</sub>	88	86	860
2	Zr(O <sup><i>n</i></sup> Bu) <sub>4</sub>	9	8	80
3	Hf(O <sup><i>n</i></sup> Bu) <sub>4</sub>	20	16	160
4	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	78	77	770

<sup>a</sup> % Conversion is the % of aldehyde converted to imine and is obtained from <sup>1</sup>H NMR of the crude product.

<sup>b</sup> All yields are wt% with respect to aldehyde after 96 h of reaction.

### 2.5. Reaction of aldimine with carbon dioxide in the presence of Ti(O<sup>*n*</sup>Bu)<sub>4</sub>

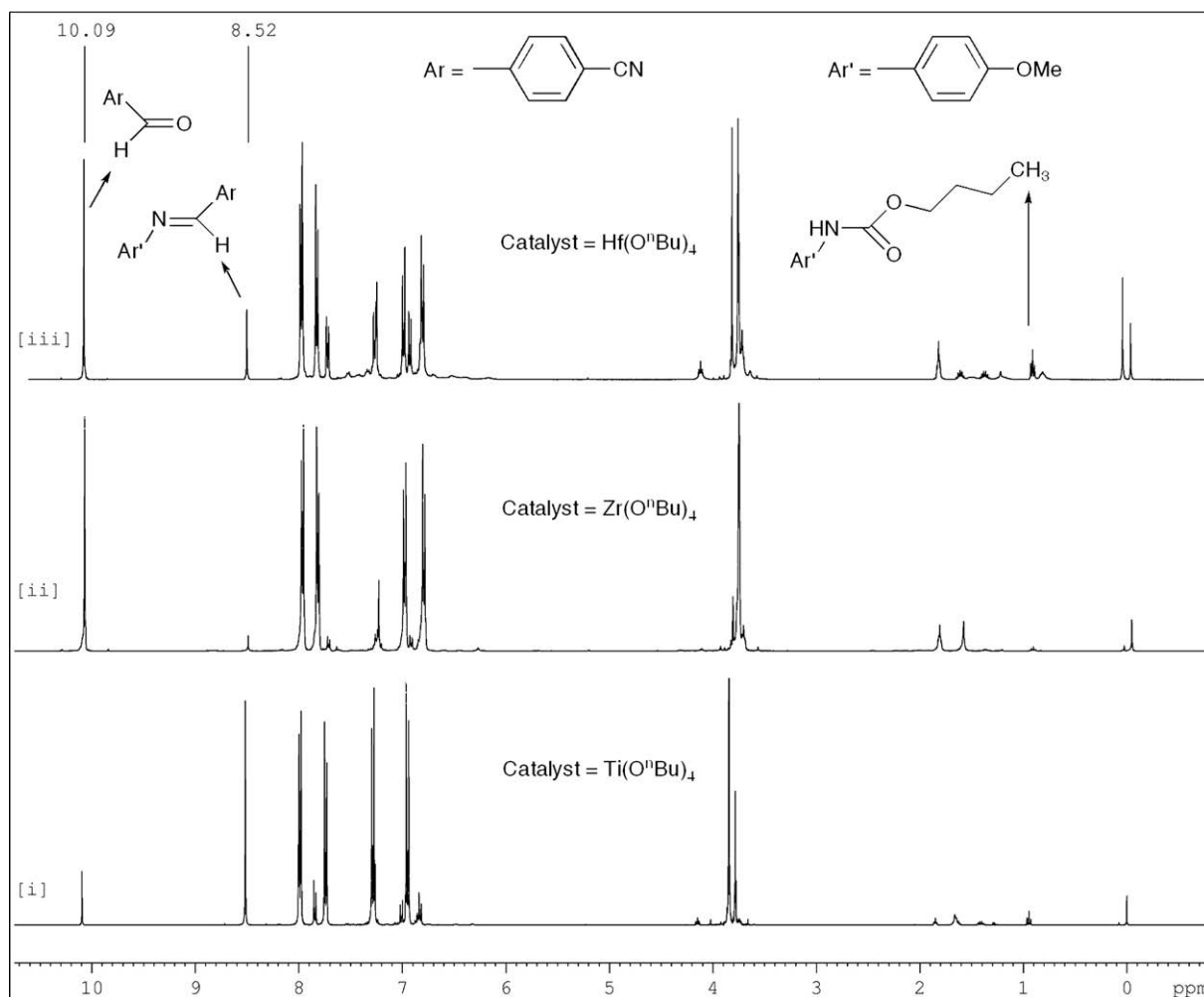
A reverse reaction with carbon dioxide (Scheme 5) was attempted. Aldimine **3a** was treated with one equivalent of Ti(O<sup>*n*</sup>Bu)<sub>4</sub> in the presence of 6 equivalents of carbon dioxide. The reaction was carried out in a sealed vial using toluene as solvent at 180 °C for 72 h. However the reaction did not proceed to completion and only 12% conversion to the metathesis product benzaldehyde was observed. The other product phenyl isocyanate was only isolated as the insertion product **4** in an equivalent amount with respect to benzaldehyde.

Earlier it has been shown that if the metathesis of heterocumulenes with carbon dioxide has to take place then it requires insertion of at least one of the substrate into the Ti–O bond and

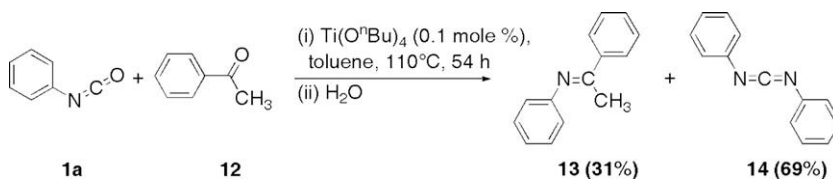
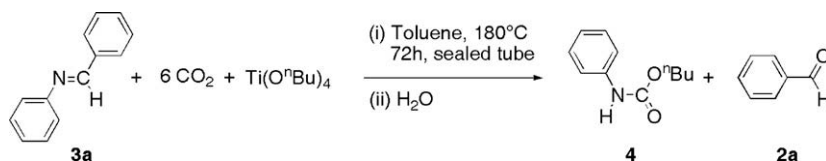
coordination of the other [6e]. It is also known that the insertion reaction of carbon dioxide with titanium(IV) isopropoxide takes place only in the presence of one fourth equivalents of water [12]. In this study it has been found that the imine never undergoes insertion into the Ti–O bond. Hence both the substrates aldimine **3a** and carbon dioxide are capable of only coordinating to the Ti centre. This results in low yields of the metathesis products. These observations clearly indicate that insertion is the key step to metathesis reaction.

### 2.6. Reaction of phenyl isocyanate with acetophenone in the presence of Ti(O<sup>*n*</sup>Bu)<sub>4</sub>

The metathesis reaction could not be extended to ketones (Scheme 6). Phenyl isocyanate did not react with acetophenone at room temperature. However at 110 °C, the expected metathesis reaction occurred with the formation of the carbodiimide. The reaction was followed by IR and after 54 h of reflux, the band at 2250 cm<sup>-1</sup> corresponding to –N=C=O stretch of isocyanate had completely disappeared and a prominent band at 2137 cm<sup>-1</sup> was observed. This corresponds to the –N=C=N– stretch of the carbodiimide. NMR analysis indicated that the product contained 69% of carbodiimide and 31% of ketimine. The carbodiimide was isolated as diphenyl urea in 60% yield after work up. At this temperature, the carbodiimide was formed as a major product and arises due to metathesis of isocyanates [6e].



**Fig. 1.** Comparison of <sup>1</sup>H NMR spectra of the crude products formed in the reaction of *p*-methoxyphenyl isocyanate with *p*-cyanobenzaldehyde in the presence of 0.1 mol% of (i) titanium(IV) *n*-butoxide, (ii) zirconium(IV) *n*-butoxide and (iii) hafnium(IV) *n*-butoxide.



### 3. Computational studies

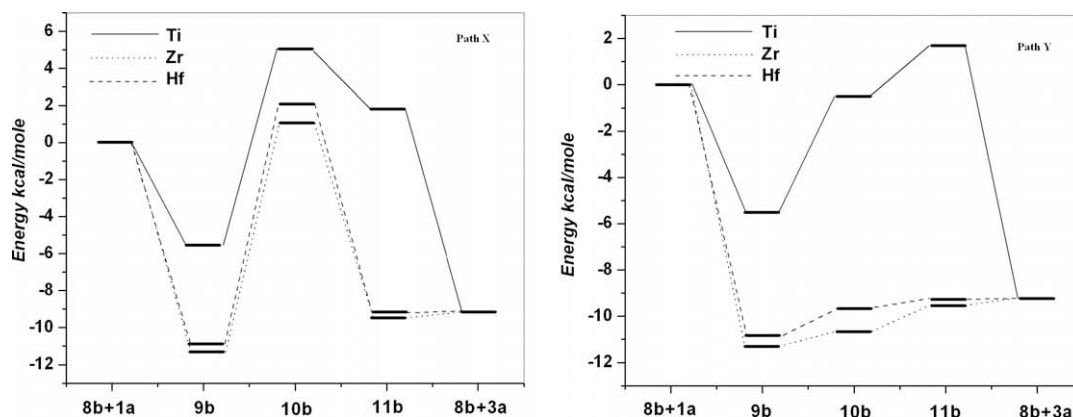
#### 3.1. Comparison of energies of intermediates for the two possible paths

Following the recent successful prediction of reactivity patterns in group(IV) metal alkoxides using computational methods [10b,13], we sought reasons for the excellent activity of Ti vs. Zr and Hf. The structures numbered **8–11** in Scheme 1 were investigated. For this purpose  $\text{Ti}(\text{O}^t\text{Bu})_4$  (**8aTi**),  $\text{Zr}(\text{O}^t\text{Bu})_4$  (**8aZr**) and  $\text{Hf}(\text{O}^t\text{Bu})_4$  (**8aHf**) were modeled by  $\text{Ti}(\text{OMe})_4$  (**8bTi**),  $\text{Zr}(\text{OMe})_4$  (**8bZr**) and  $\text{Hf}(\text{OMe})_4$  (**8bHf**) where bulky  $^t\text{Bu}$  groups are replaced by Me groups to reduce computational load. The letters **a** and **b** are used to indicate metal complexes with  $\text{O}^t\text{Bu}$  ligand and OMe ligand, respectively. **Ti**, **Zr** and **Hf** are added to indicate the metal present in the complex. For example, **10aTi** implies structure **10** with  $M = \text{Ti}$  and  $\text{O}^t\text{Bu}$  as the alkoxy group.

There are two pathways for which various intermediates are given in Fig. 2 (path **X** and path **Y**) along with the computed energy levels. The reaction of  $\text{PhNCO}$  with **8bTi** leads to the formation of a stable intermediate **9bTi**. The formation of **9bZr/9bHf** is energetically more favored by 6.0 kcal/mol than the formation of **9bTi**. Subsequent insertion of aldehyde can take place either through path **X** requiring the cleavage of  $\text{C}_2\text{--N}_1$  bond (see complex **9** in Table 4) or through path **Y** requiring the cleavage of  $\text{C}_2\text{--O}_3$  bond. If the reaction proceeds through path **X**, the energy required for formation

of **10b** is much higher in the case of zirconium and hafnium in comparison with Ti. On the other hand, if the reaction proceeds through path **Y**, the energy required for formation of **10b** and **11b** is higher for Ti. Irrespective of the path followed, the formation of aldimine **3a** with the regeneration of **8bTi/8bZr/8bHf** by the reaction of trigonal bipyramidal **9bTi/9bZr/9bHf** with  $\text{PhCHO}$  is an energetically favored process for Ti. In the case of Zr and Hf, the intermediate **9b** is more stable than the products according to the calculation. This makes the metathesis reaction with titanium alkoxide catalytically feasible but not with Zr or Hf alkoxide.

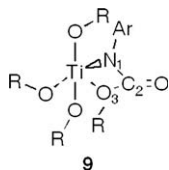
The C–O (bond between the carbonyl carbon and alkoxy oxygen in the carbamate group) and C–N bond distances of the optimized structure **9** for isocyanates with varying electronic demands were compared (Table 4). In all cases, the C–O bond (bond between the carbonyl carbon and alkoxy oxygen in the carbamate group) was found to be weaker than the normal C–O bond. The C–N bond had partial double bond character. This indicates that the reaction is likely to proceed through path **Y** that involves insertion of aldehyde into the C–O bond to give **10'**. The electronic effects of groups present on aryl isocyanates on the rate of the reaction can also be explained if we consider the reaction to occur via path **Y**. For isocyanates with electron donating group, the C–O bond was much weaker compared to those with an electron withdrawing group. This is consistent with the greater reactivity observed for isocyanates with electron donating groups.



**Fig. 2.** Computed energy profile for the reaction of phenyl isocyanate with benzaldehyde in the presence of  $\text{M}(\text{OMe})_4$  (**8b**,  $M = \text{Ti, Zr, Hf}$ ) through path **X** and path **Y** done at the B3LYP/LANL2DZ level of theory.

**Table 4**

Comparison of the C–N and C–O bond distances in intermediate **9** for isocyanates with varying electronic demands computed at the B3LYP/LANL2DZ level of theory.



Entry	Complex	Ar	$d(\text{C}_2\text{-O}_3)$ (Å)	$d(\text{C}_2\text{-N}_1)$ (Å)
1	<b>9bTiO</b>		1.49	1.35
2	<b>9bTi</b>		1.45	1.36
3	<b>9bTiF</b>		1.44	1.36

#### 4. Conclusions

A catalytic room temperature metathesis reaction of aromatic aldehydes and aryl isocyanates has been discovered. The metathesis reaction proceeds via insertion of an alkoxide into a heterocumulene. Contrary to conventional synthesis of imines from aldehydes and amines where water is the by-product, this method involves only carbon dioxide elimination. This makes water sensitive and heat sensitive aldimines accessible through this route. Titanium alkoxides were found to promote catalytic metathesis (isocyanates and aldehydes) more efficiently than zirconium alkoxides and hafnium alkoxides. Computational studies on model metal alkoxides done at the B3LYP/LANL2DZ level of theory are helpful in understanding this reactivity pattern and the reaction path. There are two ways by which metathesis could be formally achieved. The reactivity pattern for substituted isocyanates is consistent with an insertion into the C–O bond (bond between the carbonyl carbon and alkoxy oxygen in the carbamate group). Based on computational results, it is likely that the C–O bond breaks and inserts an aldehyde. The insertion product formed by Zr and Hf complex is extremely stable compared to that formed by Ti. Subsequent insertion of aldehyde to give imine is computed to be energetically unfavorable for Zr and Hf but not for Ti. This explains why titanium alkoxides are better metathesis catalysts in comparison with their heavier congeners.

#### 5. Experimental

##### 5.1. General

All manipulations were carried out under an inert atmosphere of dry nitrogen using a standard double manifold. Tetrahydrofuran was freshly distilled from sodium/benzophenone prior to use. Zirconium(IV) *n*-butoxide (84 wt% in 1-butanol), titanium(IV) *n*-butoxide, titanium(IV) isopropoxide, hafnium(IV) *n*-butoxide, phenyl isocyanate, benzaldehyde, *p*-anisaldehyde, *p*-cyanobenzaldehyde, salicylaldehyde, *p*-methoxyphenyl isocyanate, *p*-fluorophenyl isocyanate and acetophenone were obtained from Aldrich USA. The butanol solution of zirconium(IV) *n*-butoxide was evaporated to dryness under vacuum at 110 °C prior to use.

##### 5.2. Physical measurements

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AMX 400 operating at 400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR, with tetramethylsilane as internal reference. All spectra were recorded in  $\text{CDCl}_3$ .

##### 5.3. Metathesis reaction of phenyl isocyanate and benzaldehyde using stoichiometric amounts of titanium(IV) *n*-butoxide (100 mol%)

Phenyl isocyanate (0.035 g, 0.3 mmol) and benzaldehyde (0.03 g, 0.3 mmol) were mixed in dry THF (10 ml) and to this solution was added  $\text{Ti}(\text{O}^i\text{Bu})_4$  (100  $\mu\text{l}$ , 0.3 mmol). The reaction mixture was stirred at room temperature for 60 h. It was quenched by a stoichiometric amount of water (10  $\mu\text{l}$ , 0.6 mmol) and stirred for 1 h. The solvent was then removed under vacuum to give a solid residue. This residue contains **3a** and **4**. Their ratio in the crude product was determined by  $^1\text{H}$  NMR. These compounds were separated by preparative TLC using 1% ethyl acetate in petroleum ether as eluent. Yield of imine **3a** = 0.010 g (18%).

##### 5.4. Metathesis reaction of phenyl isocyanate and benzaldehyde using substoichiometric amounts of titanium(IV) *n*-butoxide (25 mol%)

Phenyl isocyanate (0.035 g, 0.3 mmol) and benzaldehyde (0.03 g, 0.3 mmol) were mixed in dry THF (10 ml) and to this solution was added  $\text{Ti}(\text{O}^i\text{Bu})_4$  (25  $\mu\text{l}$ , 0.075 mmol). The reaction mixture was stirred at room temperature for 60 h. It was quenched by a stoichiometric amount of water (2.5  $\mu\text{l}$ , 0.15 mmol) and stirred for 1 h. The solvent was then removed under vacuum to give a solid residue. This residue contains **3a** and **4**. Their ratio in the crude product was determined by  $^1\text{H}$  NMR. These compounds were separated by preparative TLC using 1% ethyl acetate in petroleum ether as eluent. Yield of the imine **3a** = 0.013 g (24%).

##### 5.5. Metathesis reaction of phenyl isocyanate and benzaldehyde using substoichiometric amounts of titanium(IV) *n*-butoxide (10 mol%)

Phenyl isocyanate (0.035 g, 0.3 mmol) and benzaldehyde (0.03 g, 0.3 mmol) were mixed in dry THF (10 ml) and to this solution was added  $\text{Ti}(\text{O}^i\text{Bu})_4$  (10  $\mu\text{l}$ , 0.03 mmol). The reaction mixture was stirred at room temperature for 60 h. It was quenched by a stoichiometric amount of water (1  $\mu\text{l}$ , 0.06 mmol) and stirred for 1 h. The solvent was then removed under vacuum to give a solid residue. This residue contains **3a**, **4** and **5**. Their ratio in the crude product was determined by  $^1\text{H}$  NMR. These compounds were separated by preparative TLC using 1% ethyl acetate in petroleum ether as eluent. Yield of the imine **3a** = 0.023 g (44%).

##### 5.6. Metathesis reaction of phenyl isocyanate and benzaldehyde using catalytic amounts of titanium(IV) *n*-butoxide (1 mol%)

Phenyl isocyanate (0.35 g, 2.9 mmol) and benzaldehyde (0.31 g, 2.9 mmol) were mixed in dry THF (10 ml) and to this solution was added  $\text{Ti}(\text{O}^i\text{Bu})_4$  (10  $\mu\text{l}$ , 0.03 mmol). The reaction mixture was stirred at room temperature for 60 h. It was quenched by a stoichiometric amount of water (1  $\mu\text{l}$ , 0.06 mmol) and stirred for 1 h. The solvent was then removed under vacuum to give a solid residue. This residue contains **3a** and trace amount of **4**. Their ratio in the crude product was determined by  $^1\text{H}$  NMR. The solid was dissolved in petroleum ether containing 1% ethyl acetate and passed through a silica plug. The solvent was then removed by distillation under reduced pressure to give the imine **3a**. Yield of the imine **3a** = 0.383 g (72%).

Similar procedure was used for the metathesis of other imines and aldehydes with varying electronic demands to obtain imines **3b–j** and the corresponding yields are given in Table 2.

### 5.7. Metathesis reaction of phenyl isocyanate and benzaldehyde using catalytic amounts of titanium(IV) *n*-butoxide (0.1 mol%)

Phenyl isocyanate (0.35 g, 2.9 mmol) and benzaldehyde (0.31 g, 2.9 mmol) were mixed in dry THF (10 ml) and to this solution was added  $\text{Ti}(\text{O}^i\text{Bu})_4$  (1  $\mu\text{l}$ , 0.003 mmol). The reaction mixture was stirred at room temperature for 60 h. It was quenched by a stoichiometric amount of water (0.1  $\mu\text{l}$ , 0.006 mmol) and stirred for 1 h. The solvent was then removed under vacuum to give a solid residue. This residue contains **3a** and trace amount of **4**. Their ratio in the crude product was determined by  $^1\text{H}$  NMR. The solid was dissolved in petroleum ether containing 1% ethyl acetate and passed through a silica plug. The solvent was then removed by distillation under reduced pressure to give the imine **3a**. Yield of the imine **3a** = 0.404 g (76%).

### 5.8. Metathesis reaction of *p*-methoxyphenyl isocyanate and *p*-cyanobenzaldehyde using catalytic amounts of titanium(IV) *n*-butoxide (0.1 mol%)

*p*-Methoxyphenyl isocyanate (0.43 g, 2.9 mmol) and *p*-cyanobenzaldehyde (0.38 g, 2.9 mmol) were mixed in dry THF (10 ml) and to this solution was added  $\text{Ti}(\text{O}^i\text{Bu})_4$  (1  $\mu\text{l}$ , 0.003 mmol). The reaction mixture was stirred at room temperature for 60 h. It was quenched by a stoichiometric amount of water (0.1  $\mu\text{l}$ , 0.006 mmol) and stirred for 1 h. The solvent was then removed under vacuum to give a solid residue. The solid was dissolved in petroleum ether containing 1% ethyl acetate and passed through a silica plug. The solvent was then removed by distillation under reduced pressure to give the imine **3e**. Yield of the imine **3e** = 0.581 g (86%).

When the same reaction when repeated with 0.1 mol% of titanium(IV) isopropoxide, zirconium(IV) *n*-butoxide and hafnium(IV) *n*-butoxide the yields of imine **3e** were 77%, 8% and 16%, respectively. Comparison of the  $^1\text{H}$  NMR spectra of the crude product for these reactions that indicate the % conversion of aldehyde **2e** to the imine to **3e** are given in Fig. 1 and Table 3.

### 5.9. Reaction of *N*-(benzylidene)aniline with carbon dioxide in the presence of titanium(IV) *n*-butoxide

Into 8 ml THF in a sealable vial flushed with nitrogen, carbon dioxide (117.0 ml, 4.8 mmol) from a gas burette was condensed. A mixture of titanium(IV) *n*-butoxide (0.3 ml, 0.8 mmol) and *N*-(benzylidene)aniline (0.16 g, 0.8 mmol) in 2 ml THF was added while maintaining the vial under liquid nitrogen. The vial was subsequently evacuated and sealed. The sealed vial was heated in an oil bath maintained at 180 °C for 72 h. The vial was broken open and the reaction mixture evacuated to dryness under vacuum. The mixture was then worked up by addition of stoichiometric amount of water (to precipitate out  $\text{TiO}_2$ ), followed by extraction of organic fraction with dichloromethane. Solvent was then evaporated to dryness from organic fraction.  $^1\text{H}$  NMR analysis of the crude product indicated that the reaction did not proceed to completion and only 12% conversion to the metathesis product benzaldehyde **2a** was observed. The other product phenyl isocyanate **1a** was only isolated as the insertion product **4** in an equivalent amount.

## 5.10. Spectral data

### 5.10.1. Compound **3a**: *N*-(benzylidene)aniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.50 (s, 1H),  $\delta$  7.95 (d, 2H,  $J = 4.0$  Hz),  $\delta$  7.48 (d, 3H,  $J = 4.0$  Hz),  $\delta$  7.45 (t, 2H,  $J = 8.0$  Hz),  $\delta$  7.28 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  160.50, 152.11, 136.23, 131.44, 129.33, 129.20, 125.99, 120.91.

### 5.10.2. Compound **3b**: *N*-(4-methoxybenzylidene)aniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.36 (s, 1H),  $\delta$  7.83 (d, 2H,  $J = 8.0$  Hz),  $\delta$  7.35 (m, 2H),  $\delta$  7.18 (m, 3H),  $\delta$  6.95 (d, 2H,  $J = 8.0$  Hz),  $\delta$  3.84 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  162.20, 159.71, 152.24, 130.50, 129.21, 129.15, 125.56, 120.80, 114.13, 55.47.

### 5.10.3. Compound **3c**: *N*-(4-cyanobenzylidene)aniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.49 (s, 1H),  $\delta$  8.00 (d, 2H,  $J = 6.4$  Hz),  $\delta$  7.76 (d, 2H,  $J = 6.4$  Hz),  $\delta$  7.41 (m, 2H), 7.23 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  158.38, 151.48, 140.42, 133.03, 129.82, 129.60, 127.43, 121.44, 118.98, 114.85.

### 5.10.4. Compound **3d**: *N*-(4-cyanobenzylidene)-4-fluoroaniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.49 (s, 1H),  $\delta$  7.99 (d, 2H,  $J = 8.0$  Hz),  $\delta$  7.75 (d, 2H,  $J = 12.0$  Hz),  $\delta$  7.24 (m, 2H),  $\delta$  7.09 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  163.07, 160.62, 157.48, 146.98, 139.86, 132.58, 129.08, 122.60, 118.41, 116.24, 116.01, 114.52.

### 5.10.5. Compound **3e**: *N*-(4-cyanobenzylidene)-4-methoxyaniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.52 (s, 1H),  $\delta$  7.98 (m, 2H),  $\delta$  7.73 (m, 2H),  $\delta$  7.29 (m, 2H),  $\delta$  6.94 (m, 2H),  $\delta$  3.84 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  159.24, 155.51, 143.84, 140.43, 132.62, 128.96, 124.53, 122.64, 118.67, 114.72, 114.06, 55.65.

### 5.10.6. Compound **3f**: *N*-benzylidene-4-methoxyaniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.47 (s, 1H),  $\delta$  7.90 (m, 2H),  $\delta$  7.45 (m, 3H),  $\delta$  7.23 (m, 2H),  $\delta$  6.92 (m, 2H),  $\delta$  3.81 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  158.30, 144.91, 136.47, 131.04, 128.75, 128.52, 122.21, 114.30, 55.47.

### 5.10.7. Compound **3g**: *N*-(4-methoxybenzylidene)-4-methoxyaniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.39 (s, 1H),  $\delta$  7.82 (d, 2H,  $J = 6.8$  Hz),  $\delta$  7.21 (d, 2H,  $J = 8.8$  Hz),  $\delta$  6.96 (d, 2H,  $J = 7.2$  Hz),  $\delta$  6.92 (d, 2H,  $J = 6.8$  Hz),  $\delta$  3.85 (s, 3H),  $\delta$  3.81 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  162.48, 158.39, 145.75, 130.73, 129.97, 122.56, 114.83, 114.63, 55.97, 55.89.

### 5.10.8. Compound **3h**: *N*-(4-methoxybenzylidene)-4-fluoroaniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.34 (s, 1H),  $\delta$  7.83 (d, 2H,  $J = 6.8$  Hz),  $\delta$  7.16 (m, 2H),  $\delta$  7.07 (m, 2H),  $\delta$  6.98 (d, 2H,  $J = 7.2$  Hz),  $\delta$  3.86 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  162.78, 160.27, 148.85, 130.97, 129.59, 122.75, 122.67, 116.38, 116.16, 114.70, 55.91.

### 5.10.9. Compound **3i**: *N*-benzylidene-4-fluoroaniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  8.46 (s, 1H),  $\delta$  7.89 (m, 2H),  $\delta$  7.44 (m, 3H),  $\delta$  7.19 (m, 2H),  $\delta$  7.07 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  162.94, 160.69, 148.53, 136.54, 131.96, 129.29, 122.84, 122.77, 116.47, 116.25.

### 5.10.10. Compound **3j**: *N*-(2-hydroxybenzylidene)aniline

$^1\text{H}$  NMR (400 MHz)  $\delta$  13.29 (s, 1H),  $\delta$  8.63 (s, 1H),  $\delta$  7.42 (m, 4H),  $\delta$  7.30 (m, 3H),  $\delta$  7.02 ( $\delta$ , 1H,  $J = 8.0$  Hz),  $\delta$  6.93 (t, 1H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  162.73, 161.15, 148.53, 133.19, 132.32, 129.45, 126.94, 121.21, 119.23, 119.11, 117.29.

### 5.10.11. Compound **4**: butyl *N*-phenylcarbamate [10]

$^1\text{H}$  NMR (400 MHz)  $\delta$  7.37 (d, 2H,  $J = 8$  Hz),  $\delta$  7.30 (t, 2H,  $J = 8$  Hz),  $\delta$  7.05 (t, 1H,  $J = 7.3$  Hz),  $\delta$  6.63 (s, 1H, NH),  $\delta$  4.17 (t, 2H,  $J = 6.7$  Hz),  $\delta$  1.65 (m, 2H),  $\delta$  1.42 (m, 2H),  $\delta$  0.95 (t, 3H,  $J = 7.3$  Hz).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  153.78, 138.02, 129.10, 123.37, 118.63, 65.18, 31.02, 19.14, 13.30.

### 5.10.12. Compound **5**: butyl 2,4-diphenylallopphanate [10]

$^1\text{H}$  NMR (400 MHz)  $\delta$  10.91 (s, 1H, NH),  $\delta$  7.53 (d, 2H,  $J = 7.6$  Hz),  $\delta$  7.41 (m, 3H),  $\delta$  7.31 (t, 2H,  $J = 7.6$  Hz),  $\delta$  7.22 (d, 2H,  $J = 7.6$  Hz),  $\delta$  7.09 (t, 1H,  $J = 7.6$  Hz),  $\delta$  4.15 (t, 2H,  $J = 6.8$  Hz),  $\delta$  1.48 (m, 2H),  $\delta$

1.18 (m, 2H),  $\delta$  0.82 (t, 3H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  156.08, 151.58, 137.77, 137.10, 128.96, 128.70, 128.26, 123.96, 119.92, 67.22, 30.31, 18.78, 13.47.

### 5.11. Computational details

For theoretical studies,  $\text{Ti}(\text{OMe})_4$ ,  $\text{Zr}(\text{OMe})_4$  and  $\text{Hf}(\text{OMe})_4$  were taken as model complexes in place of  $\text{Ti}(\text{O}^i\text{Bu})_4$ ,  $\text{Zr}(\text{O}^i\text{Bu})_4$  and  $\text{Hf}(\text{O}^i\text{Bu})_4$  where bulky  $^i\text{Bu}$  groups are replaced by Me groups for computational efficiency. All structures were optimized using the DFT method (B3LYP/LANL2DZ), based on Becke's three-parameter functional [14]. The LANL2DZ basis set uses the effective core potentials (ECP) of Hay and Wadt [15]. The nature of the stationary points was characterized by vibrational frequency calculations. The GAUSSIAN 03 program package was used for all calculations [16].

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.044.

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