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Differing Reactivities of Zirconium and Titanium Alkoxides with Phenyl Isocyanate: An Experimental and Computational Study

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The insertion reaction of 1 and 2 equiv of PhNCO (**2**) into Ti(O^{n}Bu)$_4$ (**1aTi**) and Zr(O^{n}Bu)$_4$ (**1aZr**) results in the formation of a carbamate ligand (PhNCOO^{n}Bu) referred to as a monoinsertion ligand (MIL). Reaction of metal *n*-butoxide (**1a**) with more than 2 equiv of PhNCO leads to the competitive insertion of PhNCO into the M−N bond of metal carbamate or into the M−O bond of the alkoxide. The ligand formed by the insertion of PhNCO into a metal carbamate is an allophanate ligand (PhNCONPhCOO^{n}Bu), referred to as a double insertion ligand (DIL). The complexes containing these ligands were hydrolyzed, and the organic products **5** (from MIL) and **6** (from DIL) were spectroscopically characterized. The reactivity of Ti(O^{n}Bu)$_4$ is very similar to the reactivity of Ti(O^{i}Pr)$_4$ reported earlier by us. The formation of DIL over MIL is clearly favored in the case of Ti(O^{n}Bu)$_4$, whereas the formation of DIL is less favored with Zr(O^{n}Bu)$_4$. At −80 °C, Zr(O^{n}Bu)$_4$ gives only MIL, and so only **5** is isolated on hydrolysis. In contrast, Ti(O^{n}Bu)$_4$ initially produces DIL and then it slowly decays to MIL, and both **5** and **6** are isolated on hydrolysis. The unusual preference for monoinsertion or double insertion has been probed computationally using model complexes Ti(OMe)$_4$ (**1bTi**) and Zr(OMe)$_4$ (**1bZr**) at the B3LYP/LANL2DZ level of theory. The relative thermodynamic stabilities of the intermediate model metal complexes (**10b**, **11b**, **12b**, and **13b**) are indicative of the diverse behavior shown by Ti and Zr. The barrier for the formation of **11bZr** is assigned to a high-energy intermediate **10bZr**, which results in the reduced preference for DIL formation. The smaller size of Ti precludes higher coordination numbers; thus the heptacoordinated intermediate **12bTi** is higher in energy compared to **12bZr**. This facilitates the formation of MIL in the case of Zr(O^{n}Bu)$_4$.

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.[1,2] A good understanding of this key step would help to control this reaction and enable the 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.[3]

Insertions of polar heterocumulenes into M−N,[4] M−C,[5] and M−O[6] have been studied with a variety of metals, especially with titanium[7,8] and zirconium.[9] The initial product of insertion could react further with another molecule of the heterocumulene, leading to multiple insertions. While there are many instances where multiple insertions occur with alkynes,[10] they have not been extensively explored in the case of heterocumulenes.[11] Multiple insertions in this context are of three types as illustrated (Scheme 1) using R′NCO insertions into M−OR: (1) reaction where insertion of more than one substrate takes place into more than one group in a metal complex (eq a); (2) reaction where

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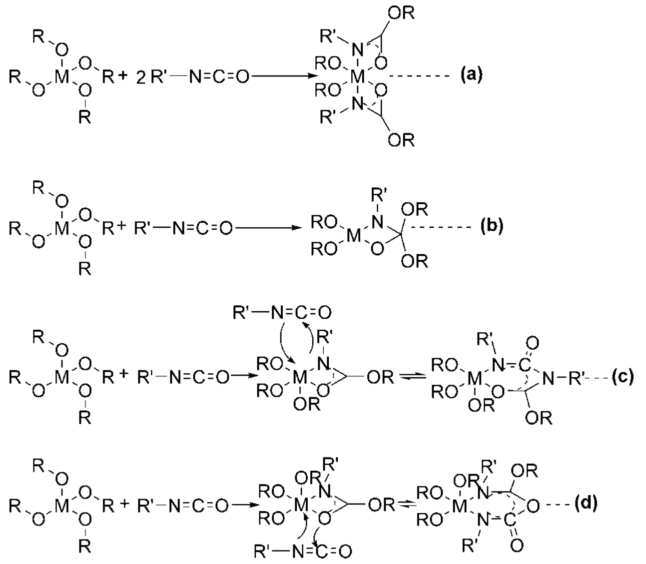
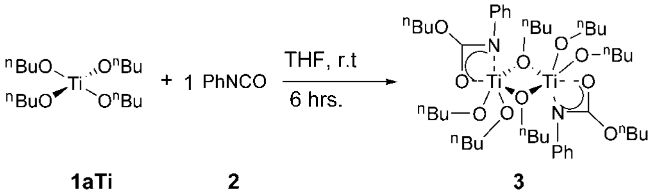
Scheme 1. Types of Reactions through Which Multiple Insertions Occur



insertion of one substrate takes place into more than one group in a metal complex (eq b); (3) reaction where insertion of more than one substrate takes place into one group in a metal complex (eqs c and d); multiple insertions according to the third pathway can further take place in either head-to-tail (eq c) or head-to-head fashion (eq d).

Well-characterized multiple insertions are mainly those of alkynes,[10a,12,13] which undergo insertion by eq a, whereas carbon disulfide,[14] nitriles,[15] isocyanides,[16a,17] and carbon monoxide[18] undergo multiple insertion by eq b. Apart from these unusual double insertions, a few examples of alkenes that show only double insertions and not polymerization are also known.[19] Surprisingly, very few complexes obtained by insertion of isocyanates and isothiocyanates into metal alkoxides have been structurally characterized.[20] Head-to-tail insertion (eq c) occurs with heterocumulenes[21a,16b–d] and alkynes,[12] and head-to-head insertion (eq d) occurs with heterocumulenes[21b] and isocyanides.[16a]

Scheme 2. Formation of Dimeric Complex 3 by the Insertion of PhNCO into Ti(O^{n}Bu)$_4$



This study reports the experimental observation of the differences in the reaction of Ti(O^{n}Bu)$_4$ and Zr(O^{n}Bu)$_4$ with PhNCO. Theoretical calculations were performed on the model complexes Ti(OMe)$_4$ and Zr(OMe)$_4$ at the B3LYP/LANL2DZ level of theory to get an insight into these reactions. The structures are numbered from **1** to **13**. The letters **a** and **b** are used to indicate metal complexes with a O^{n}Bu ligand and a OMe ligand, respectively. **Ti** and **Zr** are added to indicate the metal present in the complex. For example, **10aTi** implies structure **10** with M = Ti and O^{n}Bu as the alkoxy group.

Results and Discussion

The insertion reaction of one molecule of PhNCO (**2**) is discussed first. This is followed by the discussion of double insertion. The concentration profiles of DIL and MIL are discussed next, showing the difference in the reactivities of Ti(O^{n}Bu)$_4$ (**1aTi**) and Zr(O^{n}Bu)$_4$ (**1aZr**). Results of the computational studies with model substrates are given at the end.

Monoinsertion of Phenyl Isocyanate. The reaction of PhNCO with titanium isopropoxide has been reported to give a dimeric complex due to a facile insertion reaction.[21a] It has been characterized by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction studies. The reaction of Ti(O^{n}Bu)$_4$ with 1 equiv of PhNCO was carried out in tetrahydrofuran in a similar fashion and is expected to give the analogous product (**3**) where one of the butoxide groups at each metal center has undergone insertion (Scheme 2). ^{1}H NMR of this reaction mixture in CDCl$_3$ was recorded and found to contain three resonances at 4.15, 4.24, and 4.45 ppm. These peaks are assigned to the methylene protons adjacent to oxygen on each of the three different

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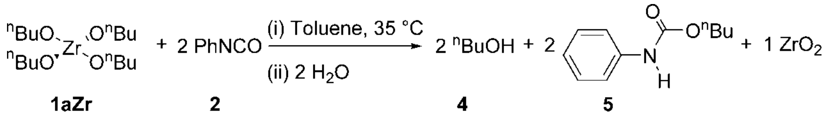
Scheme 3. Insertion of 2 equiv of PhNCO into Zr(O^{n}Bu)$_4$ Leading to 5 after Hydrolysis



Scheme 4. Insertion of more than 2 equiv of PhNCO into Zr(O^{n}Bu)$_4$ leading to 5 and 6 after Hydrolysis

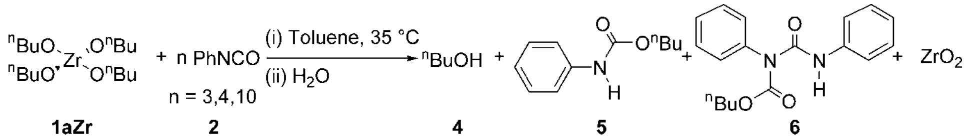


Table 1. Ratio of Hydrolyzed Products in the Reaction of Zr(O^{n}Bu)$_4$ with Varying Amounts of PhNCO in Toluene, as Shown in Scheme 4

			ratio of products (%)		
entry	equiv of **2**	time (h)	**4**	**5**	**6**
1	2	22	50	50	
2	3	27	22	71	7
3	4	30	18	64	18
4	10	48		39	61

n-butoxide groups, i.e., the carbamate (obtained by insertion of PhNCO into Ti(O^{n}Bu)$_4$), bridging and terminal, respectively. The distinctive resonances in $CDCl_3$ are consistent with the dimeric structure predicted for this complex (**3**).

The reaction of Zr(O^{n}Bu)$_4$ with 1 equiv of PhNCO resulted in a similar insertion reaction, but distinctive methylene resonances were not discernible in the NMR spectrum. Reaction of Zr(O^{n}Bu)$_4$ with 2 equiv of PhNCO leads to the formation of a product mixture with an even more complex ^{1}H NMR pattern. As products in this reaction could not be separated and characterized, the ratio of various insertion products was obtained by hydrolyzing with water. On hydrolysis, ^{1}H NMR of the solution showed only two sets of methene resonances at 3.64 and 4.17 ppm assigned to the butanol (**4**) and butyl group of butyl *N*-phenyl carbamate (**5**) in the ratio of 1:1 (Scheme 3). This shows that the reaction mixture indeed has two isocyanate groups inserted into two of the butoxides on zirconium.

Double Insertion of Phenyl Isocyanate. The reaction of Zr(O^{n}Bu)$_4$ with 3 equiv of PhNCO was carried out at 35 °C, and the reaction mixture was analyzed by ^{1}H NMR after hydrolysis. ^{1}H NMR of the products showed peaks for the butyl *N*-phenyl carbamate (**5**) and butyl 2,4-diphenylallophanate (**6**) (Scheme 4). The latter arises from the protonation of DIL, which is formed by the addition of a second molecule of PhNCO to the coordinated carbamate. The ratio of these products for different amounts of PhNCO are given in Table 1. With the increasing amounts of PhNCO, the product **6** arising from double insertion of PhNCO increased. A mechanistic scheme depicting the formation of various products, including possible intermediates, is given in Scheme 5.

Kinetic Studies. Previous results with insertion reactions of titanium(IV) isopropoxide showed that the concentration of MIL and DIL varied as a function of time.[21a] The concentration of the product arising from the double insertion of aryl isocyanates on Ti(O^{i}Pr)$_4$ decreases with time. A kinetic preference for the formation of the double-insertion product and thermodynamic preference for the monoinsertion product were suggested as possible reasons for the observed concentration profiles.[21a] A similar result is expected with Ti(O^{n}Bu)$_4$ also.

The reaction of Ti(O^{n}Bu)$_4$ with 3 equiv of PhNCO at 35 °C leads to the formation of a mixture of products containing **10aTi** (or its isomer **11aTi**) and **12aTi** (or its isomer **13aTi**) (Scheme 5). The concentrations of these compounds were estimated by hydrolysis with stoichiometric quantities of water and ^{1}H NMR analysis. While **11aTi** having MIL and DIL would give **5** and **6** in the ratio 1:1, hydrolysis of **13aTi** would give 3 equiv of **5** (Scheme 6). The ratio of **5** to **6** is a measure of the relative concentration of **10aTi** (or **11aTi**) and **12aTi** (or **13aTi**). The reaction was followed initially at intervals of 1 h and later at intervals of 3 h. The concentration of **6** reached a maximum and then showed a steady decay, whereas concentration of **5** increased with time. Ultimately the reaction mixture had only 3 equiv of MIL and one equiv of butoxide coordinated to titanium after 54 h. This suggests that **11aTi** with coordinated DIL has transferred one of the phenyl isocyanates into metal butoxide to form the complex **13aTi**, with three coordinated MIL. Such a decay can be explained by the reversibility of the step leading to **11aTi** so that the thermodynamically more stable **13aTi** is formed (Scheme 5). A similar concentration profile in the formation and decay of DIL was observed when Ti(O^{n}Bu)$_4$ was treated with 4 equiv of PhNCO at 35 °C (Figure 1).

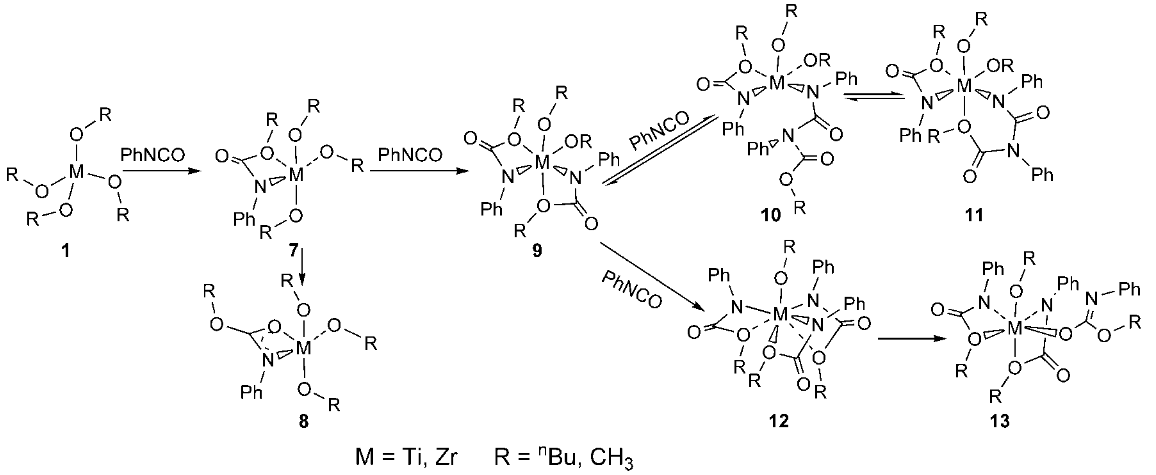
In the reaction of Zr(O^{n}Bu)$_4$ with 4 equiv of PhNCO at 35 °C, the concentration of **5** and **6** obtained after hydrolysis showed a different trend from what was seen with Ti(O^{n}Bu)$_4$. The concentration of **6** increased initially (Figure 1) and remained constant after 30 h; the concentration of **5** also showed an initial rise before remaining constant after 30 h. This implies that both **11aZr** (or **10aZr**) and **13aZr** (or **12aZr**) are formed through independent pathways and **11aZr** does not decay to **13aZr**.

Since the reactions of Ti and Zr are clearly different, there is a possibility that the kinetically favored product obtained with Ti is not favored with Zr. In order to confirm this, reactions were carried out at different temperatures. At 45 °C the reaction of Zr(O^{n}Bu)$_4$ with 4 equiv of PhNCO produced a concentration profile similar to what was observed at 35 °C (Figure 2). However, the ratios of **13aZr** to **11aZr** were different, leading to the observed concentration profiles of **5** and **6** shown in Figure 2. In the reaction of Zr(O^{n}Bu)$_4$ with 4 equiv of PhNCO at 0 °C, significantly less double insertion was observed (Figure 3).

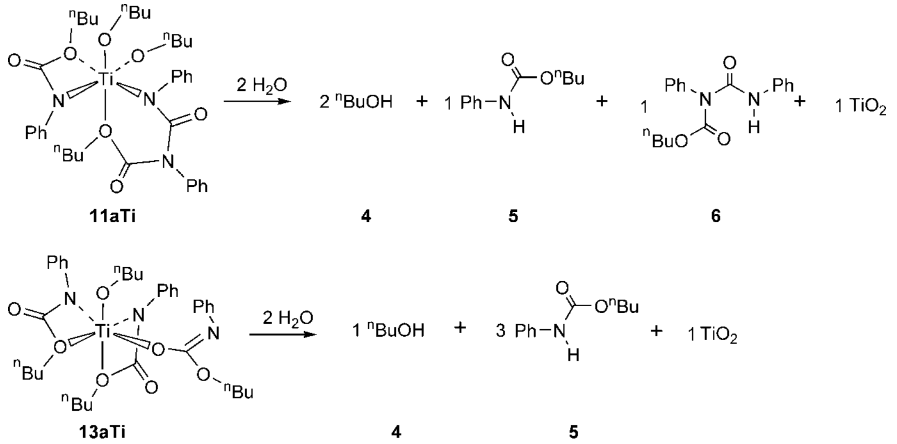
Not surprisingly, further lowering the temperature to −80 °C resulted in the formation of only **5** after hydrolysis of the reaction mixture. The concentration of **5** increased initially and remained constant after 48 h. This clearly indicates that MIL is kinetically favored in comparison to the formation of DIL. This explains the changes in the concentration of DIL and MIL as a function of temperature.

The insertion of a third molecule of PhNCO to the compound **9a** is possible either into the carbamate or into the alkoxide ligand (Scheme 5). The preference of Zr and Ti for the two insertions is different. Furthermore, the conversion of DIL to MIL as a function of time, which is observed with titanium

Scheme 5. Schematic Representation of the Stepwise Insertion of PhNCO (2) into M(OR)$_4$ Showing the Intermediates Involved



Scheme 6. Hydrolysis Products of the Intermediates Involved in the Reaction of Ti(O^{n}Bu)$_4$ with 3 equiv of PhNCO



alkoxides, is not observed in the reaction of zirconium alkoxide. To explain these differences, a theoretical study was undertaken. The difference in reactivity of Ti and Zr had been observed in several other reactions, and computational studies have helped in understanding the differences.[22]

Computational Studies

Support for the mechanistic scheme and the product ratios was sought from computational studies. For this purpose, Ti(O^{n}Bu)$_4$ (**1aTi**) and Zr(O^{n}Bu)$_4$ (**1aZr**) were modeled by Ti(OMe)$_4$ (**1bTi**) and Zr(OMe)$_4$ (**1bZr**), where bulky ^{n}Bu groups are replaced by Me groups for easy computation (Scheme 5). Experimentally, insertion of 2 equiv of PhNCO into metal *n*-butoxide (**1a**) gives only MIL. This implies that the first two steps (**1** → **7** → **9**) involve insertion of PhNCO into the metal alkoxide bonds. The insertion of one molecule of PhNCO into the M−O bond of **1b** leads to a carbamate ligand coordinated through N and the oxygen of the alkoxide. This gives structure **7b**, which presumably rearranges to **8b**. In the case of titanium isopropoxide, insertion of PhNCO leads to the analogue of **8b**, which was isolated as a dimer and crystallographically characterized.[21a] It is worth noting that the energy difference between the two species **7b** and **8b** is quite small (1.1 kcal/mol).

The reaction of octahedral metal complex **9b** with PhNCO leads to the square-pyramidal intermediate **10b** (insertion into carbamate) or heptacoordinated **12b** (insertion into alkoxide by [2+2] cycloaddition), which subsequently gives octahedral **11b** or **13b**, respectively. Since **11b** gives DIL and MIL in the ratio 1:1 whereas **13b** gives 3 equiv of MIL, the ratio of **11b**/**13b**

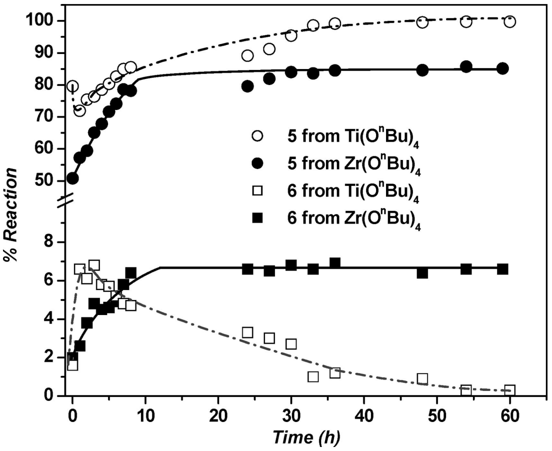


Figure 1. Formation of insertion products **5** and **6** in the reaction of Ti(O^{n}Bu)$_4$ and Zr(O^{n}Bu)$_4$ with 4 equiv of PhNCO in THF at 35 °C.

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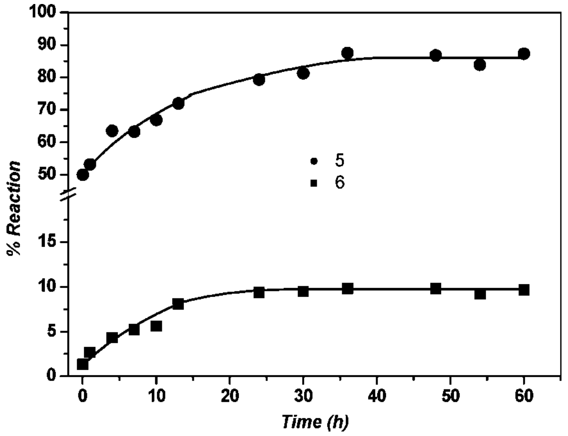

Figure 2. Formation of insertion products **5** and **6** in the reaction of $Zr(O^nBu)_4$ with 4 equiv of PhNCO in THF at 45 °C.

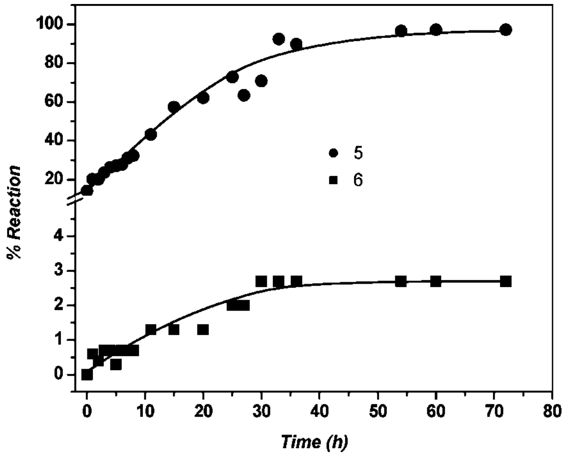

Figure 3. Formation of insertion products **5** and **6** in the reaction of $Zr(O^nBu)_4$ with 4 equiv of PhNCO in THF at 0 °C.

determines the ratio of DIL/MIL. So the key questions that we need to answer are the following. Are there differences in the thermodynamic stabilities of **11b** and **13b** for Ti and Zr? If so, are these reflected in the ratios of products? In the reaction of **9b** with PhNCO, does the metal prefer formation of **10b** or **12b** (precursors to **11b** and **13b**, respectively), and if so, why?

The energetics for the formation of various intermediates is given in Figure 6 for Ti and Zr. In the reaction of $Ti(OMe)_4$, formation of square-pyramidal **10bTi** appears to be an uphill process. Rearrangement to octahedral **11bTi** leads to a more stable product. Similarly, formation of **11bZr** is preceded by the high-energy intermediate **10bZr**. However, in comparison to the Ti intermediate, the Zr intermediate is higher in energy. This makes it understandable why the reaction of Ti leading to **11bTi** is reversible but the corresponding reaction of Zr is not reversible.

The energetics of the reaction leading to the formation of **12b** and **13b** give further insight into the product profiles observed in the reactions of Ti and Zr. In the case of Zr, formation of **12bZr** is a downhill process (Figure 4). The corresponding reaction of Ti leading to the stable **13bTi** is preceded by an intermediate **12bTi**, which is heptacoordinated and higher in energy. On the other hand, the heptacoordinated structure **12bZr** is more stable compared to **13bZr/10bZr**. Therefore, the **12bZr** will be formed more readily in the reaction compared to **10bZr/11bZr** or **13bZr**. But the smaller Ti does not show this preference for the heptacoordinated **12bTi**. The preference of Zr for a larger number of ligands as in **12b** is a well-precedented observation documented in other systems.[22]

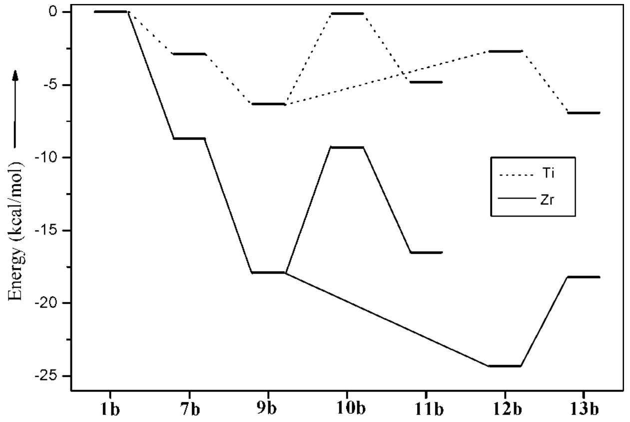

Figure 4. Reaction energy profile for the insertion of 3 equiv of PhNCO (**2**) into $M(OMe)_4$ (**1b**, M = Ti, Zr), indicating the relative energies of the intermediates.

Thermodynamic stabilities computed for the model substrates are extremely valuable in understanding the differences in product profiles. Although intermediate **13bTi** is thermodynamically more stable than **11bTi**, the energy difference between the two intermediates is only 1.7 kcal/mol. The reversibility of these reactions is indicated by the formation of both **5** and **6** (hydrolysis products of **13Ti** and **11Ti**, respectively) in the beginning followed by slow decrease in the concentration of **6** with concomitant increase in the concentration of **5**. In contrast, the formation of **11Zr** involves a thermodynamically higher energy intermediate **10Zr**. This prevents the formation of **11Zr** and consequently isolation of **6** on hydrolysis of the reaction mixture at low temperatures. Since the reverse reaction would follow the same pathway, the decay of **11Zr** to **12Zr** is unfavorable. The intermediate **12Zr**, however, is very stable, making it the more favorable product at low temperatures. Hydrolysis of **12Zr** leads to isolation of **5**.

Conclusions

Recent studies with insertion reactions of $Ti(O^iPr)_4$ and heterocumulenes have shown that heterocumulenes CO_2, PhNCO, and PhNCS behave in a very similar fashion. However, there are significant differences in the reactivity of Ti and Zr toward phenyl isocyanate. Computational studies on model metal alkoxides are helpful in understanding this reactivity pattern. The difference in reactivity is primarily attributed to the difference in size of the two metals; Zr prefers higher coordination numbers. Reactions leading to seven coordinated complexes are stabilized more in the case of Zr than in the case of Ti. This explains why only monoinsertion takes place with Zr at low temperatures. The double insertion of **2** results in an intermediate that involves formation of five-coordinated species. This process is computed to be energetically unfavorable for Zr but not as much for Ti, a fact that is borne out by the experimental observation regarding reversibility of double insertion in the case of titanium alkoxides.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of dry argon using a standard double manifold. Toluene and tetrahydrofuran were freshly distilled from sodium/benzophenone prior to use. Zirconium(IV) *n*-butoxide (84 wt % in 1-butanol) and titanium(IV) *n*-butoxide were obtained from Aldrich

USA. Butanol was removed from zirconium *n*-butoxide solution under vacuum at 110 °C. Phenyl isocyanate was obtained from Merck and used as supplied.

Physical Measurements. ^{1}H NMR and ^{13}C{H} NMR were recorded on a Bruker AMX 400 operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, with tetramethylsilane as internal reference. All spectra were recorded in CDCl$_3$. HRESMS was recorded on a Micromass ESI-TOF MS instrument.

Synthesis of 3. Titanium(IV) *n*-butoxide (0.1 mL, 0.29 mmol) was dissolved in 6 mL of tetrahydrofuran, and to this solution phenyl isocyanate (0.32 mL, 0.29 mmol) was added. The mixture was stirred at room temperature for 6 h. The solvent was evaporated to dryness under vacuum to obtain an orange solid (0.10 g, 79%). ^{1}H NMR (400 MHz): δ 7.36 (m, 8H), 7.15 (m, 2H), 4.15 (t, 4H, $J = 7.6$ Hz), 4.24 (t, 4H, $J = 6.8$ Hz), 4.45 (t, 8H, $J = 6.8$ Hz), 1.5–1.8 (m, 32 H), 0.9 (m, 24H). ^{13}C NMR (100 MHz): δ 153.74, 148.76, 139.77, 129.45, 128.54, 123.52, 118.55, 67.77, 67.61, 65.00, 31.02, 30.84, 30.72, 19.19, 19.10, 18.96, 13.86, 13.56, 13.48.

Kinetic Measurements. Reaction of 1aZr with 4 equiv of 2 at −80 °C. Zirconium(IV) *n*-butoxide (0.14 g, 0.37 mmol) was dissolved in 10 mL of tetrahydrofuran. This solution was kept in an acetone/dry ice bath maintained at −80 °C. After 45 min of equilibration, phenyl isocyanate (0.16 mL, 1.48 mmol) was added. The mixture was stirred at −80 °C for 72 h. The reaction was monitored at regular intervals by transferring aliquots of 0.1 mL into an NMR tube, decomposing by addition of water, removal of solvent under vacuum, and product dissolution in CDCl$_3$ before ^{1}H NMR analysis. To this sample was then added known amounts *p*-bromoacetophenone as an internal standard. Concentrations of organic products **5** and **6** were estimated from integrals of methene protons of ligand with respect to methyl protons of the internal standard. The procedures for other kinetic experiments are similar and are given in the Supporting Information.

Compound 5, Butyl *N*-phenyl carbamate[23a]. Zirconium(IV) *n*-butoxide (0.14 g, 0.37 mmol) was dissolved in 10 mL of tetrahydrofuran. To this solution was added phenyl isocyanate (0.16 mL, 1.48 mmol) and stirred for 30 h. The solvent was evaporated to dryness under vacuum to yield a yellow paste. This mixture was redissolved in methylene chloride, taken in a separating funnel, and washed with distilled water, and the organic layer was extracted by evaporation. This organic layer contains **5** and **6** in the ratio 12:1. They were separated by preparative TLC using 1% ethyl acetate in petroleum ether as eluent. Compound **5**: mp = 62−63.5 °C. ^{1}H NMR (400 MHz): δ 7.37 (d, 2H, $J = 8$ Hz), 7.30 (t, 2H, $J = 8$ Hz), 7.05 (t, 1H, $J = 7.3$ Hz), 6.63 (s, 1H, NH), 4.17 (t, 2H, $J = 6.7$ Hz), 1.65 (m, 2H), 1.42 (m, 2H), 0.95 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (100 MHz): δ 153.78, 138.02, 129.10, 123.37, 118.63, 65.18, 31.02, 19.14, 13.30.

Compound 6, Butyl 2,4-diphenylallophanate[23b]. Mp = 64.5 −65.5 °C. ^{1}H NMR (400 MHz): δ 10.91 (s, 1H, NH), 7.53 (d, 2H, $J = 7.6$ Hz), 7.41 (m, 3H), 7.31 (t, 2H, $J = 7.6$ Hz), 7.22 (d, 2H, $J = 7.6$ Hz), 7.09 (t, 1H, $J = 7.6$ Hz), 4.15 (t, 2H, $J = 6.8$ Hz), 1.48 (m, 2H), 1.18 (m, 2H), 0.82 (t, 3H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz): δ 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. HRESMS: found $m/z = 335.1356$ $(M + Na)^+$, calcd mass for $C_{18}H_{20}N_2O_3Na$ is 335.1372.

Computational Details. For theoretical studies, Ti(OMe)$_4$ and Zr(OMe)$_4$ were taken as model complexes in place of Ti(O^{n}Bu)$_4$ and Zr(O^{n}Bu)$_4$, where bulky ^{n}Bu groups are replaced by Me groups for computational efficiency. All structures were optimized using the hybrid HF-DFT method, B3LYP/LANL2DZ, based on Becke's three-parameter functional[24a] including Hartree–Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke[24b] together with the nonlocal correction for the correlation energy suggested by Lee[24c] et al. The LANL2DZ basis set uses the effective core potentials (ECP) of Hay and Wadt.[25] The nature of the stationary points was characterized by vibrational frequency calculations. The Gaussian 03 program package was used for all calculations.[26]

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Supporting Information Available: Total energy, optimized Cartesian coordinates, geometries, and detailed procedures for kinetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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