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Catalytic addition reactions of amines, thiols, and diphenylphosphine oxides to heterocumulenes using a bridging Sulfonylimido titanium(IV) complex

Indrani Banerjee,^{a†} Shweta Sagar,^{a†} Christian Lorber^{*b} and Tarun K. Panda^{*a}

Abstract: We present here an efficient method for hydroelementation reactions such as hydroamination, hydrothiolation, and hydrophosphorylation of the heterocumulenes carbodiimides, aryl isocyanates, and isothiocyanates with anilines or thiophenols using a *p*-tolylsulfonylimido-supported dinuclear titanium complex. All the reactions were achieved in excellent yield under mild conditions and within a short reaction time. The products were isolated and fully characterized by spectroscopic techniques. We also propose a mechanism involving the proton abstraction (of the E-H of anilines or thiophenols) in the first step. In the reaction mechanism, the amido groups of the binuclear Ti^{IV} complex act as the leaving group whereas the sulfonylimido linkage remains unaffected.

Introduction

Synthetic chemists in recent years have given immense consideration to the insertion of readily available nucleophilic substrates selectively into the small molecules to synthesize new C-E (E= N, O, S, P) bonds.^[1,2] The newly formed C-E and C=E bonds in the small molecules pave the pathway for the generation of a variety of substituted urea, thiourea, and guanidine derivatives that possess wide applications in pharmaceutical and agricultural industries.^[3] Their applicability expands as active catalysts in organic synthesis, organometallics^[4] and also show powerful aspects in coordination, supramolecular, and materials chemistry.^[5] Hydroelementation reactions such as hydroamination, hydrophosphorylation, hydrothiolation on carbodiimides, thiocyanates and isothiocyanates affording guanidine, urea, and thiourea although aid the straight-forward and atom-economic approach, but reports are scarce.

Traditional methodologies for guanidine synthesis involve thioureas, isothioureas, amidine sulfonic acids, cyanamides, carbodiimides, triflyl guanidines, and carboximidamides.^[6] However, the limitations of acquiring the limited substrate scope and lower yields of the guanidines from the known protocols encouraged the growth of various organometallic catalysts by synthetic chemists. The area has been developed by various research groups around the globe.

Investigators observed that employing efficient metal catalysts are essential for direct guanylation reactions. The suitable catalysts were required to overcome the electrostatic repulsion between unsaturated substrates (alkenes, alkynes, carbodiimides, isocyanates/isothiocyanates) and the Lewis bases used for the various hydroelementation reactions. Although there have been remarkable contributions from several research groups around the globe for the development of these catalysts, the reaction methodologies often involve prolonged reaction time or the use of expensive rare-earth metal complexes.^[7] Alongside hydrothiolation and hydrophosphorylation on thiocyanates and isothiocyanates also emerged as beneficial reactions.^[8] To overcome the cost-effective concerns, the growth of catalysts from earth-abundant and low-cost metals was encouraged. In this regard, several research groups have focused on the synthesis of earth-abundant metal catalysts for a series of hydroelementation reactions.

Titanium being earth-abundant and less toxic than many known heavy metal catalysts has been widely developed as the beneficial catalyst.^[9] Richeson working group first introduced titanium(IV) imido complex for the guanylation reaction that produced good yields of guanidines with diversified anilines in 2003.^[10] Later on, Xie *et al.* exhibited a half-sandwich titanium-amido complex $[\{\sigma\text{-}\eta^1\text{-}\eta^2\text{-}(\text{OCH}_2)(\text{Me}_2\text{N}=\text{CH}_2)\text{C}_2\text{B}_9\text{H}_9\}\text{-Ti}(\text{NMe}_2)]$ which pioneered the functional group tolerance of guanylation by varying the acyclic to cyclic and heterocyclic amines.^[11] The same working group further utilized the catalyst for the synthesis of cyclic guanidines that displayed extensive biological activity and high coordination modes for a variety of metal centers.^[12] In recent years, Hill *et al.*, Eisen *et al.* and Westerhausen *et al.* thus documented alkali and alkaline earth metal complexes likely magnesiumimido, $[(\text{THF})_3\{\text{K}(\text{OPMe}_2)_4\}]$ and magnesium alkyl complex, $[\text{CH}\{\text{C}(\text{Me})\text{-NDipp}\}_2\text{Mg}^n\text{Bu}]$ (Dipp = 2,6-*i*-Pr₂C₆H₃) complexes which were observed as active catalysts for a series of hydroelementation reactions namely hydro-phosphorylation, hydroboration and C-C bond formation towards carbodiimides and other heterocumulenes.^[13] In our research group, several

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Text giving experimental details for the catalytic reactions, ¹H, ¹³C(¹H), ¹⁹F(¹H) and ³¹P(¹H) spectra of guanidines, urea and thioureas **2a-2k**, **3a-3s**, **4a-4d** and **5a-5c** in Supporting Information.

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group-4 metal complexes have been developed for a range of applications.^[14] A series of mononuclear and binuclear Ti(IV) complexes were developed as efficient catalysts for a series of hydroelementation reactions for the insertion of E-H bonds into heterocumulenes with broad substrate scope in ambient conditions (Figure 1).^[15]

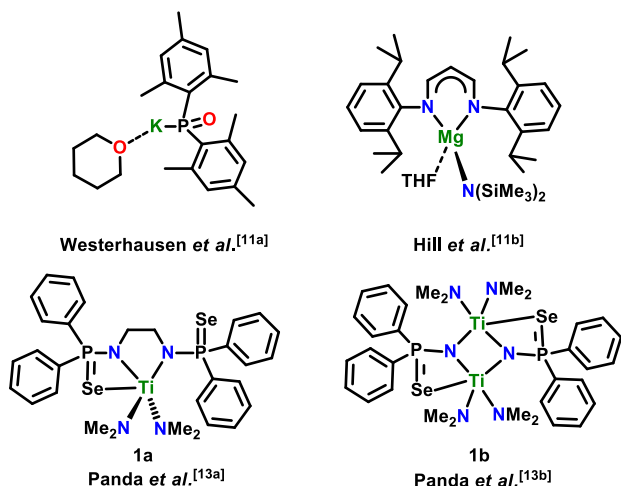
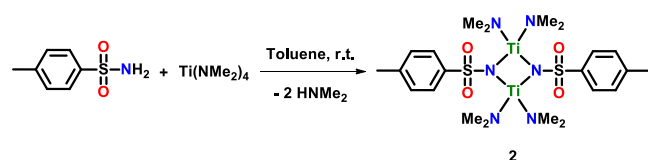


Figure 1. Selective main group and early transition metal complexes for hydroelementation reactions.

Inspired by the highly effective binuclear Ti^{IV} metal catalyst **1b** described in figure 2 for hydroelementation reactions, we chose to further examine the catalytic activity of the dinuclear titanium (IV) complex [Ti(μ -NTs)(NMe₂)₂]₂ (**2**) towards a series of E-H (E = N, S, P) additions to heterocumulenes. Complex **2** is a rare example of a sulfonylimido complex of an early transition metal.^[16] The strong electron-withdrawing groups at the two bridging imido-N atoms, make **2** extremely electron-poor which could lead to an interesting reactivity.

Results and Discussion

The titanium(IV) complex [Ti(μ -NTs)(NMe₂)₂]₂ (**2**) was synthesized according to the procedure mentioned in previous literature by Lorber *et al.* and was obtained as an orange solid (Scheme 1).^[16a] Complex **2** displayed moderate solubility in common organic solvents such as THF and toluene.

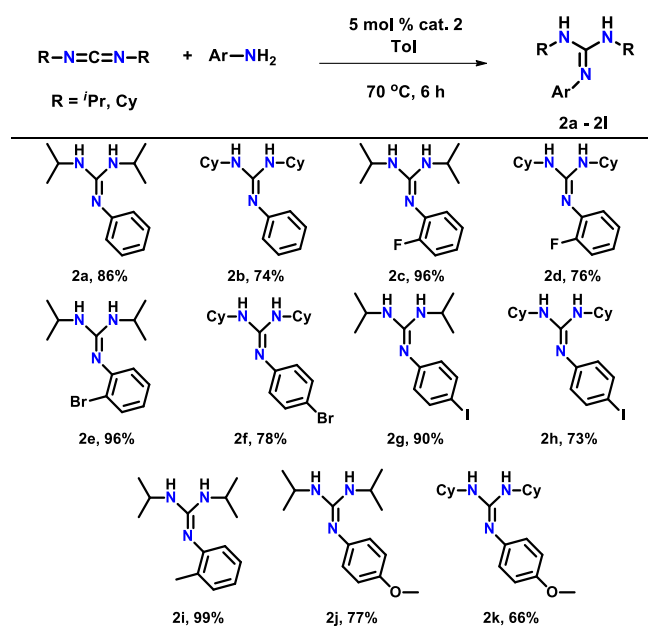


Scheme 1. Synthesis of *p*-tolylsulfonamide supported titanium(IV) complex **2**.

The catalytic activity of complex **2**.

Initially, the catalytic hydroamination reaction was carried out on less reactive carbodiimides as the heterocumulenes with primary arylamines undergo the hydroamination process mediated by titanium catalyst **2**. The reaction of *N,N*-diisopropylcarbodiimide (DIC) with aniline was first conducted in toluene in presence of 5 mol % of catalyst **2** under an inert atmosphere at room temperature for 6 hours. The desired guanidine formation was not observed. However, when the temperature was raised to 70 °C the same reaction lead to the formation of the corresponding guanidine. The product was isolated with a good yield of 86% (Table 1, entry **2a**). A similar reaction with aniline was also performed on *N,N*-dicyclohexylcarbodiimide (DCC) which also produced a good yield of 74% of the corresponding guanidine (Table 1, entry **2b**). The insertion products were isolated and analyzed by ¹H and ¹³C{¹H} NMR spectroscopy. Thus, the reaction protocol was further subjected to DIC and DCC with a variety of aromatic amines ranging from electron-withdrawing to electron-donating substitutions. The results are set out in Table 1.

Table 1. Hydroamination reactions on carbodiimides catalyzed by **2**.^[a,b]



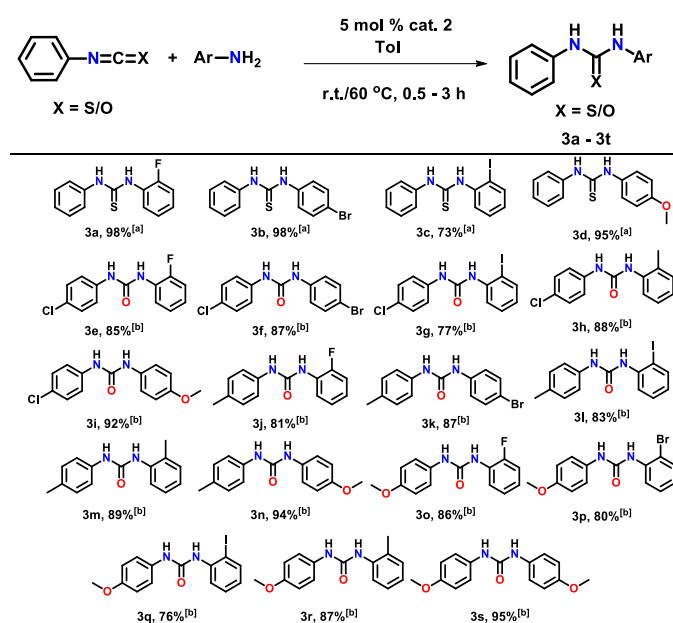
^[a] Reaction conditions: catalyst **2** (5 mol%), carbodiimides (1 eq.), amines (1 eq.). The reaction mixture was heated at 70 °C. ^[b] Isolated yield.

The N-H insertion on DIC and DCC was then carried out with electron-withdrawing halo-substituted anilines such as *o*-fluoro, *o*-bromo, *p*-bromo, and *p*-iodo aniline (Table 1, entries **2c-2h**). The guanidine derivatives achieved from DIC were obtained with better yields up to 86-96%, however, those obtained from DCC derivatives produced lower yields up to 73% probably due to the solubility issues of the reaction mixture. The reaction was subjected to DIC by amine substrate was examined by varying the electron-donating group such as *o*-toluidine and we were delighted to have isolated 99% yield of the product (Table 1, entry **2i**). The use of *p*-anisidine however was sluggish and displayed a drastic decrease in the yield of the respective guanidines (Table 1, entries **2j-2k**).

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Motivated by the results of the synthesis of guanidines, the efficacy of the binuclear Ti(IV) complex **2** was further extended for the addition of N-H bonds to more reactive aryl isocyanate and isothiocyanate derivatives. Primarily, the catalytic hydroamination protocol was carried out on phenyl isothiocyanate with *o*-fluoroaniline in toluene in presence of 5 mol % of catalyst **2** under an inert atmosphere at room temperature for two hours. An excellent yield of 98% of the corresponding thiourea was obtained (Table 2, entry **3a**).

Table 2. Hydroamination reactions on aryl isocyanates/isothiocyanates catalyzed by **2**.^[a,b]



^[a]Reaction conditions: catalyst **2** (5 mol%), isocyanates/ isothiocyanates (1 eq.), amines (1 eq.). ^[b]Isolated yield. ^[c]For **3a-3e**, reactions were carried out at r.t. for 2-3 h. ^[d]For **3f-3s**, reactions were carried out at 60 °C for 15-30 mins.

The N-H addition on phenyl isothiocyanate by other halo-substituted anilines such as *p*-bromo and *o*-iodo aniline were subjected and the hydroamination product was achieved in excellent yields respectively (Table 2, entries **3b-3c**). The molecular structure of **3b** was confirmed from a single-crystal X-ray analysis (Figure 2). On the other hand, electron-donating substrates *p*-anisidine on phenyl isothiocyanate provided the corresponding thioureas with an excellent 95% (Table 2, entry **3d**).

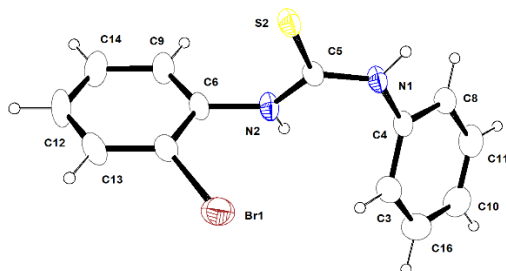
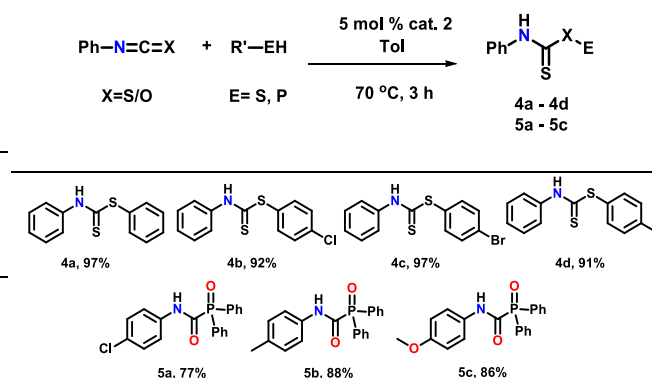


Figure 2. The solid-state structure of thiourea product **3b**. Hydrogen atoms besides N-H bonds are omitted for clarity. CCDC No. 2176204.

The catalytic hydroamination was expanded to various aryl isocyanate derivatives. A range of urea products was isolated from the reaction protocol by varying the substitutional changes on both phenyl isocyanate and amine substrates promoted by catalyst **2** in toluene for 15-30 minutes by employing a temperature of 60 °C. The reaction of *o*-fluoro, *p*-bromo, and *o*-iodo aniline on *p*-chlorophenyl isocyanate under optimal conditions produced moderate to good yield up to 87% (Table 2, entries **3e-3g**). The use of *o*-toluidine and *p*-anisidine on *p*-chlorophenyl isocyanate for the hydroamination reaction again exhibited a better yield of up to 92% (Table 2, entries **3h-3i**). Next, the reaction was examined on *p*-tolyl isocyanate with electron-withdrawing *o*-fluoro, *p*-bromo, and *o*-iodo aniline substrates. Very good yields of the urea derivatives were obtained (Table 2, entries **3j-3l**). The urea derivatives were isolated in quantitative yields by carrying out the hydroamination reaction between *o*-toluidine and *p*-anisidine with *p*-tolyl isocyanate (Table 2, entries **3m-3n**), as well as with *p*-methoxyphenyl isocyanate and various amine substrates (Table 2, entries **3o-3s**). The catalytic reaction was extended to observe the formation of corresponding ureas and thioureas utilizing secondary amines. However, successful product formation was not observed although reaction conditions were altered. This catalytic methodology was limited to primary amines.

Table 3. Addition of E-H (E = S/P) to aryl isocyanates/-isothiocyanates.^[a,b]



^[a]Reaction conditions: catalyst **2** (5 mol%), isocyanates/ isothiocyanates (1 eq.), thiols/diphenyl-phosphine oxide (1 eq.). ^[b]Isolated yield.

After obtaining a range of hydroamination products from heterocumulenes, the catalyst efficiency was further extended to hydroalkoxylation and hydrothiolation on phenyl isocyanate and isothiocyanate derivatives. The addition of O-H bonds on phenyl isothiocyanates was checked with ethanol and phenol. However, the reaction was sluggish and only a trace amount of products were obtained. On the other hand, the addition of the S-H bond of thiophenol to phenyl isothiocyanate for carrying out catalytic hydrothiolation reaction displayed interesting results when

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promoted by 5 mol % of catalyst **2**. The results are given in Table 3.

The corresponding phenylcarbamdithioate product was isolated in 97% yield within three hours at 70 °C in toluene (Table 3, entry **4a**). The reaction of *p*-chloro and *p*-bromo thiophenol with phenyl isothiocyanate afforded the addition products 4-chlorophenyl phenylcarbamdithioate and 4-bromophenyl phenylcarbamdithioate, respectively, in excellent yields (Table 3, entries **4b-4c**). The 4-methoxyphenyl phenylcarbamdithioate derivative obtained from the electron-donating *p*-methoxy thiophenol as a substrate was also produced in a quantitative yield (Table 3, entry **4d**).

Furthermore, the addition of P-H bonds to phenyl isocyanate derivatives was studied under similar reaction conditions. The reaction between diphenylphosphine oxide and *p*-chlorophenyl isocyanate, *p*-tolyl isocyanate, and *p*-methoxyphenyl isocyanate led to the formation of the *N*-(4-chlorophenyl)-(diphenylphosphoryl)formamide, (diphenylphosphoryl)-*N*-(*p*-tolyl)formamide and (diphenylphosphoryl)-*N*-(4-methoxyphenyl)formamide which were isolated in moderate to good yields (Table 3, entry **5a-5c**). The solid-state structures of **5a** and **5c** have been established by single-crystal X-ray analysis (Figures 3 and 4).

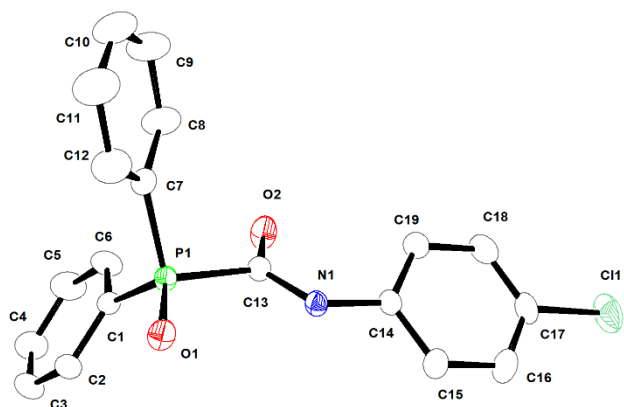


Figure 3. The solid-state structure of phosphoryl products **5a**. Hydrogen atoms besides N-H bond are omitted for clarity. CCDC No 2176205 (**5a**).

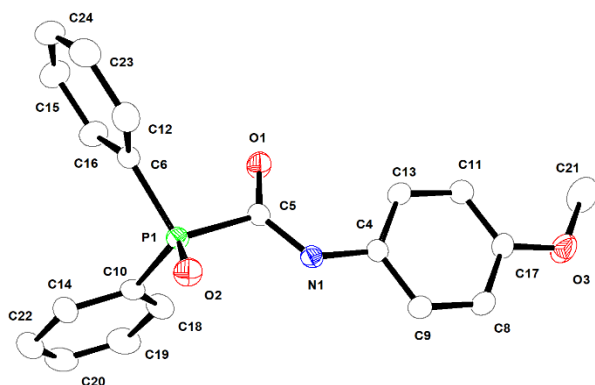
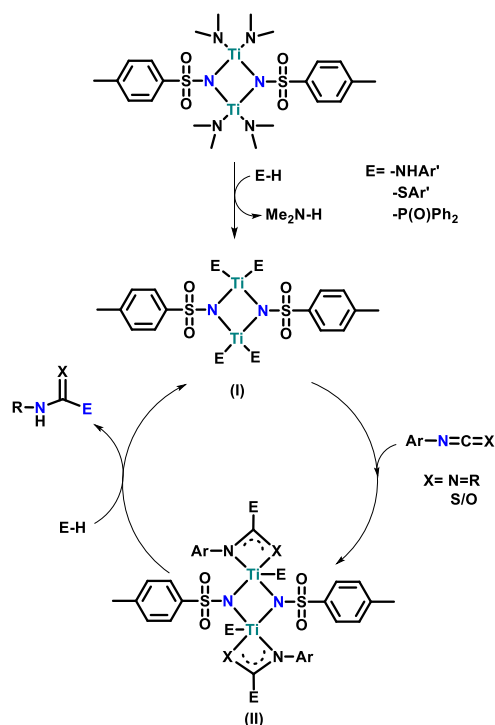


Figure 4. The solid-state structure of phosphoryl products **5c**. Hydrogen atoms besides N-H bond are omitted for clarity. CCDC No. 2176206 (**5c**).

The structural and refinement parameters of the crystal structures of **3b**, **5a**, and **5c** are given in Supporting Information. All the products were isolated as grey to white solid residues and were analyzed through ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR, and mass spectroscopy. The yields of the products were calculated from the isolated yield of the pure products.

Most plausible mechanism

A most plausible mechanism has been postulated based on the previous report by the binuclear Ti(IV) complex **1b** from our research group.^[15b] The first step in the mechanism involves the rapid protonolysis of catalyst **2** by the E-H moiety of the incoming nucleophile substrate, with the elimination of dimethylamine, forming the active pre-catalyst **I**. This first step is well documented, including for imido-amido complexes analogous to **2**, where it has been shown that substitution of several $-\text{NMe}_2$ takes place with retention of the dimeric $\text{Ti}_2(\mu\text{-imido})_2$ core structure.^[17] Migratory insertion of the heterocumulenes to the corresponding Ti-E bond of the active species takes place in the following step, generating an intermediate complex **II**. The next step involves a protonolytic cleavage with the addition of another molecule of E-H species. This completes the catalytic cycle with the release of the desired product and regeneration of the active species **I**.



Scheme 2. The most plausible mechanism of Ti(IV) complex **2** catalyzed hydroelementation reactions.

Conclusions

In summary, we have described here the use of an earth-abundant *p*-tolylsulfonylimido binuclear Ti^{IV} complex as a competent pre-catalyst for the addition of the E-H (E = N, S, and P) bond to heterocumulenes such as carbodiimides, phenyl isocyanates, and isothiocyanates. This protocol provides a convenient approach for the insertion of electron-rich amines, phosphines, and thiols into the heterocumulenes at mild reaction conditions within a short reaction time. The suggested mechanism of the catalytic addition of the nucleophilic E-H bonds to heterocumulenes involves the formation of an active Ti-E species. The catalyst showed good tolerance to functional groups allowing good to the excellent conversion of the corresponding adducts.

Experimental Section

General Experimental Procedures

All manipulations involving air- and moisture-sensitive compounds were carried out with argon, using the standard Schlenk technique or argon-filled MBraun glove box. CDCl₃ and C₆D₆ were distilled and stored in the glove box. ¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz), and ³¹P{¹H} (162 MHz) spectra were measured on a BRUKER AVANCE III-400 spectrometer. ¹H NMR spectra were recorded on a 400 MHz spectrometer at 298 K in CDCl₃ and DMSO-*d*₆ and chemical shifts (δ ppm) and coupling constants (Hz) are reported in a standard fashion regarding internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm). ¹³C{¹H} NMR spectra were recorded on a 100 MHz spectrometer at 298 K in CDCl₃ and DMSO-*d*₆ and chemical shifts (δ ppm) are reported relative to CHCl₃ [δ_C = 77.00 ppm (central line of the triplet)] and [δ_C = 39.50 ppm (central line of the septet)] respectively. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Hydrocarbon solvents (*n*-hexane, toluene) were distilled in a nitrogen atmosphere from sodium benzophenone and LiAlH₄ and stored inside the glove box. All the starting materials *N,N*-diisopropylcarbodiimide, *N,N*-dicyclohexylcarbodiimide, phenyl isocyanate, 4-chlorophenyl isocyanate, 4-tolyl isocyanate, 4-methoxyphenyl isocyanate, phenyl isothiocyanate, and the amines were purchased from Sigma Aldrich India and used without further purification. Diphenylphosphine oxide and the thiophenol derivatives were purchased from Alfa Aesar or TCI Chemicals (India) Pvt. Ltd. The titanium(IV) complex supported by a *p*-tolylsulfonylimido ligand was prepared according to the procedure reported in the literature.^[16a]

General procedure for Ti(IV) catalyzed insertion of nucleophiles (amines, thiols, and diphenylphosphine oxides) with heterocumulenes (2a-2k, 3a-3s, 4a-4d, 5a-5c). All catalytic reactions were performed using the following standard protocol. In a Schlenk flask inside the glove box, catalyst **2** (10 mg, 0.016 mmol, 5 mol %) and the respective nucleophile (0.327 mmol) dissolved in toluene (1.0 mL) were added dropwise into the reaction mixture of respective heterocumulene (0.327 mmol) in toluene. The dark red solution was kept on stirring according to the reaction conditions as mentioned in Tables 1-3. After the mentioned reaction time, the solvent was evaporated under reduced pressure to achieve white solid residue. The solid was washed three times with hexane (3 x 5 mL) and dried under a vacuum. The purified white solid was extracted from dichloromethane in the aqueous layer. The combined organic layer was collected and dried over anhydrous sodium sulfate. The collected organic layer was evaporated to obtain the corresponding products as a white solid. The products were characterized by ¹H and ¹³C{¹H} NMR spectroscopy.

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Keywords: Titanium(IV) catalyst • hydroamination • hydrothiolation • guanidine • heterocumulenes

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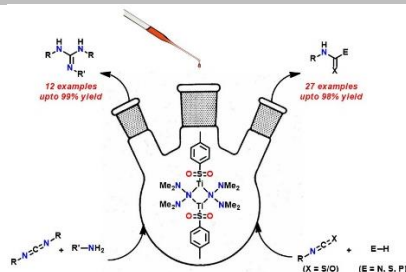
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FULL PAPER

A bridging sulfonylimido Ti^{IV} complex catalyzed addition reactions of several arylamines, thiols, and diphenylphosphine oxides with different heterocumulenes are reported.



*Indrani Banerjee, Shweta Sagar,
Christian Lorber* and Tarun K. Panda**

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Catalytic addition reactions of amines, thiols, and diphenylphosphine oxides to heterocumulenes using a bridging Sulfonylimido titanium(IV) complex

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