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Imidazolin-2-iminato Ligand-Supported Titanium Complexes as Catalysts for the Synthesis of Urea Derivatives

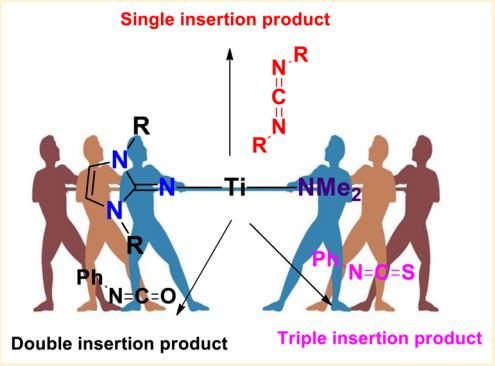
Kishor Naktode,[†] Suman Das,[†] Jayeeta Bhattacharjee,[†] Hari Pada Nayek,[§] and Tarun K. Panda*[,†]

[†]Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi Sangareddy, 502 285 Telangana, India

[§]Department of Applied Chemistry, Indian School of Mines, Dhanbad, 826004 Jharkhand, India

Supporting Information

ABSTRACT: The reactions of tetrakis(dimethylamido)titanium(IV) [Ti(NMe$_2$)$_4$] with three different imidazolin-2-imines (Im^{R}NH; R = *tert*-butyl (*t*Bu), mesityl (Mes), and 2,6-diisopropylphenyl (Dipp)) afforded the corresponding titanium imidazolin-2-iminato complexes [(Im^{R}N)Ti(NMe$_2$)$_3$] (R = *t*Bu, **1a**; R = Mes, **1b**; R = Dipp, **1c**). Treatment of complex **1a** with two different carbodiimides [R′N═C═NR′; R′ = cyclohexyl (Cy) and isopropyl (*i*Pr)] resulted in the formation of imidazolin-2-iminato titanium mono(guanidinate) complex of the type [(Im^{R}N)Ti(R′NC(NMe$_2$)NR′) (NMe$_2$)$_2$ (R′ = *i*Pr; R = *t*Bu (**2a**), R = Dipp (**2c**); R′ = Cy, R = *t*Bu (**3a**)], as yellow solid in 94% yield. However, a similar reaction of **1b** and **1c** with 2 equiv of phenyl isocyanates at ambient temperature resulted in the formation of corresponding titanium bis(ureate) complexes [(Im^{R}N)Ti{κ^2-OC(NMe$_2$)-NPh}$_2$(NMe$_2$)] (R = Mes, **4b** and R = Dipp, **4c**). Three equivalents of phenyl isothiocyanate reacted with complex **1c** to afford respective titanium tris(thioureate) complex [(Im^{Dipp}N)Ti{κ^2-SC(NMe$_2$)NPh}$_2${κ^1-SC(NMe$_2$)NPh}] (**6c**). The molecular structures of **1a**−**c**, **2a**, **2c**, **3a**, **4c**, and **6c** were established by X-ray diffraction analyses, and, from the solid-state structures of **1a**−**c**, **2a**, **2c**, **3a**, **4c**, and **6c**, it was confirmed that the imidazolin-2-iminato titanium bond in each case is very short and possesses a multiple-bonding character. The imidazolin-2-iminato titanium complex **1c** was utilized as a precatalyst for the addition of amine N−H bond to phenyl isocyanate. High yields of the corresponding urea derivatives were achieved under mild conditions. The mechanistic study of the aforementioned catalytic reaction was performed, and the active catalyst complex **7b** was isolated using 2 equiv of iminopyrrole [2-(2,6-*i*Pr$_2$C$_6$H$_3$N═CH)C$_4$H$_3$NH] and the complex **4b**. The molecular structure of **7b** was thereafter established.



INTRODUCTION

Catalytic hydroamination reactions of alkenes and alkynes as a powerful tool for the formation of C−N bonds have been studied with a wide range of transition metal and lanthanide metal complexes.[1−5] The addition of amine N−H bond to carbodiimdes using an efficient metal catalyst can provide the atom efficient route to the formation of multisubstituted guanidine.[6,7] In an analogous method, the addition of amine N−H bond to the isocyanates, using a suitable metal catalyst, produces corresponding urea derivatives.[8] Guanidine, and the substituted guanidine derivatives, are an important class of compounds present in biologically and pharmaceutically active molecules. They have received considerable attention due to their electronic and variable static effects.[9] Today, guanidine derivatives are utilized for many purposes, as they can serve as building blocks in various pharmaceutical and natural products.[10] These molecules can also act as organic bases and catalyze various organic transformations.[11] Guanidines are also used as ancillary ligands in the preparation of a variety of metal complexes including those of main, transition, and lanthanides metals.[12] Urea functional groups play important roles in organic, medicinal, supramolecular, and material chemistry.[13] Although a number of methodologies including oxidative carbonylation of amines[14] have been developed, the catalytic addition of amine N−H to an isocyanate is limited to very few metal complexes. This is in sharp contrast to the preparation of guanidine where a wide range of metal complexes are known to act as efficient catalysts.[15] Very recently, Tamm and Eisen have described the thorium complex-mediated catalytic addition of E−H bonds (E = N, P, S) to carbodiimides, isocyanates, and isothiocyanates leading to the formation of corresponding inserted products.[16]

In the reported imidazolin-2-iminato thorium(IV) alkyl complex, the role of imidazolin-2-iminato ligand was found to be very important for stabilizing the precatalyst. Monoanionic imidazolin-2-iminato ligands such as Im^{R}N$^-$ are often described by the two limiting resonance structures, thus indicating that the ability of the imidazolium ring to stabilize a positive charge leads to highly basic ligands[17] with a strong electron-donating capacity toward early transition metals.[18] Because of their ability to act as 2σ, 4π-electron donors, these ligands can be regarded as monodentate analogues of cyclopentadienyls, C$_5$R$_5$, and also as monoanionic imido ligands similar to those

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described for related phosphoraneiminato ligands.[19] This concept was successfully utilized by Tamm and co-workers to introduce imidazolin-2-iminato ligands into transition metals, lanthanide, and more recently, actinide metals to achieve very short M−N bonds.[20] We and others[19] have already established that monoanionic imidazolin-2-iminato ligands are efficient systems for the preparation of catalytically active transition metal and rare earth metal complexes.[21]

The structural characterization of rare earth metal complexes of the types $[(Im^RN)MCl_2(THF)_3]$ and $[(\eta^8\text{-}C_8H_8)M(Im^RN)(THF)_n]$ (THF = tetrahydrofuran) revealed, in all cases, the presence of terminal imidazolin-2-iminato ligands with exceptionally short metal−nitrogen bonds.[20c,h] This led to the consideration of a multiple-bonding character between M−N bonds.[22] Today, various metal complexes supported by imidazolin-2-iminato ligands display high activity in ethylene (co)polymerization and alkyne metathesis.[23]

Recently, we reported that a group 4 metal−nitrogen bond, inserted into the carbon−nitrogen double bond of carbodiimides and α-diimines to afford guanidinate and amido−imino ligand, supported group 4 metal complexes.[24] With such knowledge, we were specifically interested about the use of early transition metal complexes stabilized by monoanionic imidazolin-2-iminato ligand. We were curious to explore their catalytic activity to prepare urea derivatives by the reaction of isocyanate and amines. While some of the titanium imidazolin-2-iminato complexes such as $[(Im^RN)TiCl_3]$, $[(Im^RN)TiCpCl_2]$, and $[(Im^RN)TiCpMe_2]$ have already been reported[18c] by Tamm et al., their exploitation as a catalyst toward catalytic addition of the amine N−H bond to heterocumelens has not been reported until date.

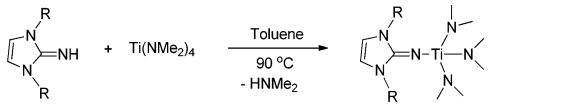
We report here the synthesis and structural details of various imidazolin-2-iminato titanium amido complexes of general formula $[(Im^RN)Ti(NMe_2)_3]$ (R = *t*Bu, **1a**; R = mesityl (Mes), **1b**; R = 2,6-diisopropylphenyl (Dipp), **1c**). We also describe the synthetic and structural aspects of various complexes like $[(Im^RN)Ti\text{-}(R'NC(NMe_2)NR')(NMe_2)_2]$ (R′ = *i*Pr; R = *t*Bu (**2a**), R = Dipp (**2c**); R′ = Cy, R = *t*Bu (**3a**)], $[(Im^RN)Ti\{\kappa^2\text{-}OC(NMe_2)NPh\}_2(NMe_2)]$ (**4c**) and $[(Im^{Dipp}N)Ti\{\kappa^2\text{-}SC(NMe_2)NPh\}_2\{\kappa^1\text{-}SC(NMe_2)NPh\}]$ (**6c**) obtained by the stoichiometric reaction of **1** with different heterocumelenes. The results of catalytic additions of different amines to the phenyl isocyanate using **1c** as the catalyst are also reported here along with the mechanistic details.

RESULTS AND DISCUSSION

Preparation and Structural Characterization of Complexes $[(Im^RN)Ti(NMe_2)_3]$ (R = *t*Bu, 1a; R = Mes, 1b; R = Dipp, 1c). Tetrakis(dimethylamido)titanium(IV) $[Ti(NMe_2)_4]$ was reacted with 1 equiv of imidazolin-2-imines (Im^RNH; R = *t*Bu, Mes, and Dipp) to afford the corresponding titanium imidazolin-2-iminato complexes $[Im^RNTi(NMe_2)_3]$ (R = *t*Bu (*tert*-butyl), **1a**; R = Mes, **1b**; R = Dipp, **1c**) as a yellow solid and in good yield. All the complexes were obtained as pure forms in good yield through recrystallization from *n*-pentane at −35 °C. All the titanium complexes showed good solubility in common organic solvents such as THF, pentane, and toluene.

Complexes **1a−c** were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectral data, combustion analysis, and single-crystal X-ray crystallography. Well-resolved NMR spectra measured in C_6D_6 were obtained for complexes **1a−c**, and each complex showed one set of ^1H and $^{13}C\{^1H\}$ NMR resonances for the $-NMe_2$ moieties. The resonances for 18 protons attached to three dimethyl amide groups appeared as a sharp singlet for each case (δ 3.37 for **1a**, 3.01 for **1b**, and 2.91 ppm for **1c**) in the ^1H NMR spectra. Additionally, complexes **1a−c** showed another singlet (δ 5.95 for **1a**, 5.68 for **1b**, and 5.92 ppm for **1c**) for the resonances of two olefinic protons present in the imidazole backbone. These chemical shift values were in the range (5.93 ppm) previously reported for $[(Im^RN)_2TiCl_2]$, $[(Im^RN)Ti(\eta^5\text{-}Cp)Cl_2]$[18a,c] and $[Im^RNLnCl_2(THF)_3]$ (Ln = Sc, Y, Lu).[20c,h] The *tert*-butyl protons in complex **1a** were observed as a sharp singlet at δ 1.58 ppm whereas the mesityl methyl protons for complex **1b** appeared as two singlets at δ 2.25 and 2.13 ppm, respectively. In complex **1c** having 2,6-diisopropylphenyl (Dipp) groups attached to the imidazol-2-imine moiety, the ^1H NMR spectrum exhibited two doublet resonances (1.41 and 1.20 ppm) having a coupling constant of 6.85 Hz each for the isopropyl CH_3 groups, thus indicating that rotation around the C−N−Ti axis is restricted. The single crystals for complexes **1a−c** were grown at −35 °C from *n*-pentane. The solid-state structures of complexes **1a−c** were established by single-crystal X-ray analysis.

Scheme 1. Syntheses of Titanium Complexes 1a−c



Im^RNH (R = *t*Bu, Mes, Dipp) R = *t*Bu (**1a**), Mes (**1b**), Dipp (**1c**)

Complex **1a** crystallizes in monoclinic space group *C*2/*c* having one molecule of **1a** along with half molecule of neutral imidazolin-2-imine ($Im^{tBu}NH$) in the asymmetric unit. However, complex **1b** crystallizes in monoclinic space group $P2_1/c$ having four molecules and complex **1c** in triclinic space group $P\bar{1}$ having two molecules in their respective unit cells. Thus, the differences in space groups observed for complexes **1a−c** could be due to the different substituents in the imidazole rings. The molecular structures of complexes **1a−c** confirmed, in each case, the coordination of imidazolin-2-iminato ligand with the titanium ion. The solid-state structure of complex **1a** is shown in Figure 1, whereas Figures FS1 and FS2 in the Supporting Information display the molecular structures of complexes **1b** and **1c**. Detailed structural and refinement parameters for complexes **1a−c** are given in Table TS1 in the Supporting Information, and selected bond lengths and angles of complexes **1a−c** are given in Table TS2 in Supporting Information. In all the complexes **1a−c**, the titanium ion is tetracoordinated with the three amido nitrogen atoms from dimethyl amides and one imido nitrogen atom from imidazolin-2-iminato moiety to adopt a distorted tetrahedral geometry around the titanium ion. The $Ti-N_{amide}$ distances in **1b** and **1c** are very similar (1.916−1.925 Å for **1b** and 1.910−1.924 Å for **1c**), while varying slightly for **1a** (1.905−1.951 Å), presumably due to the bulky *tert*-butyl substituent over imidazolium nitrogen atoms of imidazolin-2-iminato ligand.

In complex **1a**, the imidazolin-2-iminato moiety coordinates with the titanium ion in an essentially linear fashion [Ti−N3−C1 = 178.4(1)°]. Further, the $Ti-N_{iminato}$ bond length of 1.824(1) Å is in the range of observed titanium imidazolin-2-iminato complexes $[(Im^{tBu}N)Ti(\eta^5\text{-}Cp)Cl_2]$ (170.9° and 1.765 Å) and $[(Im^{tBu}N)_2TiCl_2]$ (170.9° and 1.788 Å).[18a,c] However, for complexes **1b** and **1c**, deviations from linearity are observed in coordination of Im^RN moiety [Ti−N1−C1 = 164.5(1)° and 169.2(1)°, respectively]. The $Ti-N_{iminato}$ bond lengths

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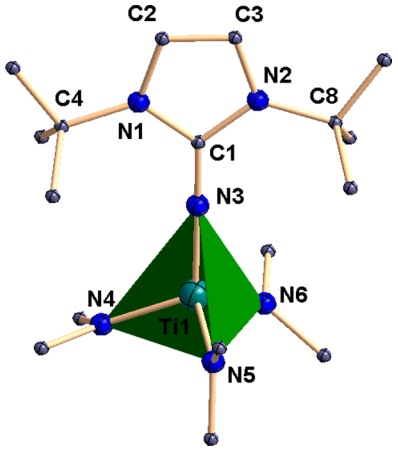
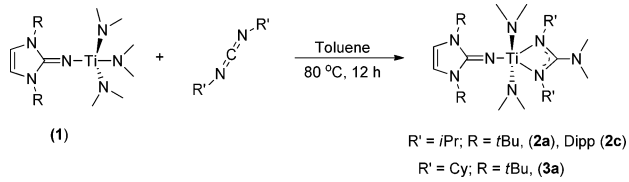


Figure 1. Molecular structure of complex **1a** showing a distorted tetrahedron polyhedron around a titanium metal ion. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: **1a**: Ti1−N3 1.824(2), Ti1−N5 1.904(2), N3−C1 1.295(2), C1−N3−Ti1 178.4, N3−Ti1−N5 105.5(8), N5−Ti1−N6 112.6(8). **1b**: Ti1−N1 1.850(1), Ti1N5 1.916(1), N1C1 1.281(2), C1N1Ti1 164.5(1), N5−Ti1−N6 111.6(6). **1c**: Ti1−N1 1.853(1), Ti−N5 1.920(2), N1−C1 1.274(2), C1−N1−Ti1 169.2(1), N5−Ti1−N6 104.9(8). More bond lengths and angles are given in Supporting Information.

[1.851(1) Å for **1b** and 1.853(1) Å for **1c**] are also slightly larger than that in **1a**. Thus, it is evident that the *tert*-butyl groups, which have positive inductive effects, reasonably enhance electron donation from imidazolin-2-iminato moiety to titanium ion as compared to the effect of electron-withdrawing aromatic substitution present in imidazolium nitrogen atoms for **1b** and **1c**. Similar observations have been made in previous reports.[18a,c]

Preparation and Structural Characterization of Titanium Mono(guanidinate) Complex [(Im^{R}N)Ti(R′NC-(NMe$_2$)-NR′)(NMe$_2$)$_2$] (R = *t*Bu; R′ = *i*Pr (2a), R = Dipp; R′ = *i*Pr (2c); R = *t*Bu; R′ = Cy (3a)). As a part of our interest in the coordination chemistry of Ti−N$_{iminato}$ complexes, we attempted the reaction of equivalent amount of *N*,*N*′-diisopropylcarbodiimide with [(Im^{R}N)Ti(NMe$_2$)$_3$] (where R = *t*Bu (**1a**) and Dipp (**1c**)). Both the reactions were performed in toluene at 80 °C. The corresponding titanium guanidinate complexes **2a** and **2c** were isolated in good yield (Scheme 2).

Scheme 2. Synthesis of Complexes 2a, 2c, and 3a



Similarly, the reaction of *N*,*N*′-dicyclohexylcarbodiimide with **1a** afforded, in good yield, the monoinserted guanidinate product [(Im$^{t\mathrm{Bu}}$N)Ti(Me$_2$NC-(NCy)$_2$)(NMe$_2$)$_2$] (**3a**; Scheme 2).

The syntheses of **2a**, **2c**, and **3a** followed a relatively easy insertion reaction, wherein one of the labile amide moieties replaced from the primary ligand sphere of the metal were inserted on the central carbon atoms of the *N*,*N*′-diisopropylcarbodiimide ligands, thus leading to the formation of monomeric imidazolin-2-iminato titanium(IV) bis-(dimethylamido) (guanidinate) complexes. Complexes **2a**, **2c**, and **3a** were characterized by standard spectroscopic analysis, and suitable crystals for single-crystal X-ray diffraction analysis were grown from concentrated toluene solution at −35 °C. ^{1}H NMR spectra for complexes **2a**, **2c**, and **3a** was recorded at 25 °C in benzene-d_6. The resonance signals, at δ 5.82 ppm (for **2a**), 5.92 ppm (for **2c**), and 5.90 ppm (for **3a**), could be assigned to the two olefinic backbone protons of Im^{R}N^{-} moiety in each complex. In addition, multiplets at δ 3.51−3.58 ppm for complex **2a** and 3.71−3.76 ppm for **2c** were observed for methine protons—*CH* of isopropyl groups from guanidine moiety. Doublet signals appeared at δ 1.12 ppm (for **2a**) and δ 1.14 ppm (for **2c**) for the methyl protons of isopropyl groups. This was well within the agreement with relative [{(*i*PrN)$_2$-CNMe$_2$}$_3$Ti(NMe$_2$)] complex as reported by us earlier.[24] For the complex **3a**, multiplets were also found at δ 3.22−3.19, 1.88−1.85, and 1.28−1.24 ppm for the resonance of corresponding methylene −*CH*$_2$ protons of the cyclohexyl groups of guanidinate moiety. Singlet resonances also appeared at δ 1.58 (for **2a**) and 1.60 ppm (for **3a**) for respective *t*Bu-protons present in the ligand fragment of respective compounds, and they were in the range similar to that of complex **1a** (1.58 ppm). However, complex **2c** displayed a doublet signal centered at δ 1.14 ppm and a multiplet centered at δ 3.46 ppm for the isopropyl groups present in the Im$^{\mathrm{Dipp}}$N^{-} moiety.

The solid-state structures of complexes **2a** and **3a** are presented in Figures 2 and 3, respectively, and the molecular

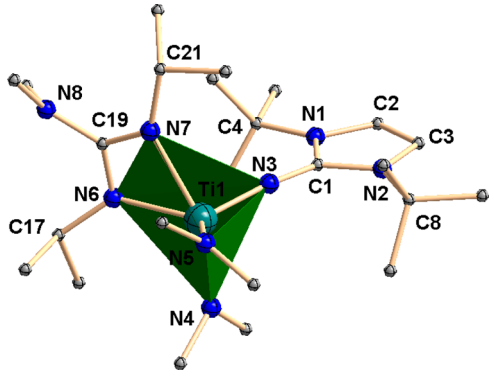


Figure 2. Solid-state structure of complex **2a** showing distorted trigonal bipyramidal polyhedron around titanium ion. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ti1−N3 1.836(4), Ti1−N4 1.952(4), Ti1−N6 2.114(4), Ti1−N7 2.192(4), C1−N3−Ti1 173.1(3), N3−Ti1−N4 98.3(2), N6−Ti1−N7 61.7(1), N6−C19−N7 111.6(5). More bond lengths and angles are given in Supporting Information.

structure of complex **2c** is given in Figure FS3 in the Supporting Information. Selected bond lengths and bond angles of complexes **2a**, **2c**, and **3a** are given in Table TS2 in Supporting Information. Detailed structural parameters for **2a**, **2c**, and **3a** are given in Table TS1. Complexes **2a**, **2c**, and **3a** carry similar structural features. Complex **2a** crystallizes in orthorhombic space group $P2_12_12_1$ having four molecules in its unit cell, whereas both the complexes **2c** and **3a** crystallize in monoclinic space group $P2_1/c$ having four molecules in their respective unit cells.

In each complex **2a**, **2c**, and **3a**, the central metal titanium(IV) ion is bonded with one nitrogen atom of

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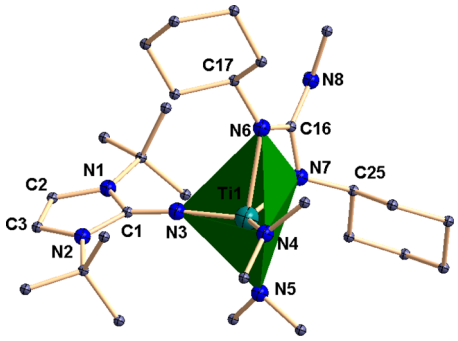


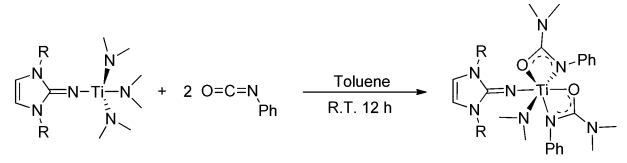
Figure 3. Solid-state structure of complex **3a** showing a distorted trigonal bipyramidal polyhedron around a titanium ion. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ti1−N3 1.838(1), Ti1−N5 1.953(1), Ti1−N6 2.276(1), Ti1−N7 2.075(1), N3−C1 1.298(2), C1−N3−Ti1 173.8(1), N3−Ti1−N5 98.0(6), N6−Ti1−N7 61.2(6), N6−C16−N7 112.7(1). More bond lengths and angles are given in Supporting Information.

Im^RN^- ligand, two nitrogen atoms from the guanidinate group, and two nitrogen atoms from two dimethyl amido moieties. The coordination geometry around the titanium(IV) ion in each case can therefore be described as a distorted trigonal bipyramidal. In the distorted trigonal bipyramidal geometry, a nitrogen atom each from the $-NMe_2$ and the guanidinate groups occupied both the apical positions, while the remaining three nitrogen atoms were located in the equatorial position (Figures 2 and 3). The Ti1−$N_{iminato}$ bond lengths in **2a** [(1.836(4) Å)], **2c** [(1.868(1) Å)], and **3a** [1.838(1) Å] were in a similar range to that of the complexes **1a** (1.8243(16) Å) and **1c** (1.853(1) Å). The bond distances between titanium and guanidinate nitrogen atoms were Ti1−N6 (2.114(4) Å) and Ti1−N7 (2.192(4) Å) for complex **2a**, whereas for complex **2c** it was Ti1−N5 (2.065(1) Å) and Ti1−N6 (2.305(2) Å) and was comparable to the corresponding distances in reported complex $[\{(iPrN)_2CNMe_2\}_3Ti(NMe_2)]$ (2.2080(6)−2.158(6) Å).[24] In complex **3a**, the delocalized π interaction within the NCN moiety (N6−C1−N7) led to partial double bonds in C−N with an average distance of 1.332 Å. Ti1−N6 and Ti1−N7 bond distances of 2.276(1) and 2.075(1) Å were comparable to the bond distances in the closely related complex $[\{(CyN)_2CNMe_2\}Ti(NMe_2)_3]$.[24]

The C−N bond lengths in the NCN fragment [N6−C1 91.355(6), N7−C19 1.315(6) Å] of complex **2a** and complex **2c** [N6−C32 1.318(2), N5−C32 1.347(3) Å] are indicative of the electron density delocalization within the guanidinate ligand. The considerably longer distances of C19−N8 [1.384(7) Å] in **2a** and C32−N8 (1.397(2) Å) in complex **2c** indicate that -NMe_2 moiety takes part in the conjugation in the guanidinate building block in the respective complexes.

Preparation and Structural Characterization of Titanium bis(ureate) Complex [(Im^RN)Ti[κ^2-OC(NMe_2)-NPh]$_2$(NMe_2)] [R = Mes (4b) and Dipp (4c)]. To study the reactivity of **1a−c** toward heterocumulenes, we performed stoichiometric reactions of complex **1** with carbodiimide, phenyl isocyanate, and phenyl isothiocyanate and isolated the stable product in each case. We found that carbodiimides could undergo monoinsertion into only the Ti−N_{amide} bond. Further, despite the presence of excess carbodiimides, complexes **2a**, **2c**, and **3a** did not undergo further reactions even at higher reaction temperatures and longer reaction times. This can be attributed to steric crowding $[\{(Cy)_2CNMe_2\}_3Ti(NMe_2)]$, since the interaction of the second carbodiimide molecule with titanium(IV) ion is prevented by the absence of a free coordination site on complex **3a** and the lower electrophiliity of the carbon center of carbodiimide molecules. In contrast, for isocyanates, a more electronegative oxygen atom can make the C═N bond more polar, thus enabling it to undergo insertion reactions. For a comprehensive study, we reacted titanium complexes **1b** and **1c** with phenyl isocyante (PhNCO) in toluene at room temperature to obtain the corresponding insertion products. A bis-insertion product of composition [(Im^RN)Ti[κ^2-OC(NMe_2)-NPh]$_2$(NMe_2)] (R = Mes, **4b** and R = Dipp, **4c**) were isolated from both 1:1 or 1:2 molar ratio of reactions indicating the higher reactivity of isocyanate toward titanium complexes **1b** and **1c**. The C═O double bond of the PhN═C═O molecule was inserted into the Ti−N bond to form the κ^2-OC(NMe_2)NPh moiety with electronic delocalization over the O−C−N unit (Scheme 3). Similar type of

Scheme 3. Syntheses of Titanium Complexes 4b and 4c



1b (R = Mes), **1c** (R = Dipp)

4b (R = Mes), **4c** (R = Dipp)

insertion reactions were reported by Xie et al. in complexes $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)(Me_2NCH_2)C_2B_9H_9]Ti[\eta^3\text{-}OC(NMe_2)\text{-}NPh]$[26] and $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]\text{-}Zr[\eta^2\text{-}OC\text{-}(NMe_2)NPh]_2$.[27]

In Fourier transform infrared (FT-IR) spectroscopy, the acyl C═O stretching frequency of **4b** and **4c** were observed at 1643 and 1640 cm^{-1}, which is substantially lower than that of the starting material phenyl isocyanate C═O (2274 cm^{-1}), thus indicating a marked decrease in C═O bond strength upon formation of the complexes **4b** and **4c**, respectively. The ^1H NMR spectrum for complexes **4b** (Figure FS3 in Supporting Information) and **4c** was recorded in benzene-d_6. The spectral data revealed that bis-insertion of phenyl isocyanate had taken place. The dimethyl amido protons shifted downfield from δ 3.01 and 2.91 ppm obtained in complexes **1b** and **1c** to δ 3.33 and 3.31 ppm obtained in complexes **4b** and **4c**, respectively; this was presumably due to coordination of two ureate moieties formed after insertion of dimethyl amide into phenyl isocyanate. Further, the migrated amido protons appeared at δ 2.10 ppm in case of complex **4b**, whereas at δ 1.56 ppm in case of **4c** as a sharp singlet. The olefinic protons of the imidazolin-2-iminato ligand backbone resonated at δ 5.65 and 5.87 ppm for complexes **4b** and **4c**, respectively, which was shifted slightly upfield from that observed in **1b** (5.68 ppm) and **1c** (5.92 ppm). In case of complex **4b**, the methyl protons of mesityl group resonate at δ 2.37 and 2.33 ppm. Whereas in case of complex **4c**, the methyl protons of isopropyl groups displayed the resonance signals as doublets centered at δ 1.20 and 1.25 ppm, respectively, with a coupling constant of 6.86 Hz each along with the methine proton of the isopropyl group resonating at δ 3.39 ppm as a broad septet. The $^{13}C\{^1H\}$ NMR spectrum displayed significant changes as compared to phenyl isocyanate (δ 134 ppm) for *ipso*-carbon of phenyl isocyanate, which appeared at δ 150.5 (**4b**) and 147.9 (**4c**) ppm, respectively. The carbonyl carbon atom resonated at 149.2 ppm, which was shifted slightly upfield to that of a similar

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complex $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OC(NMe_2)\text{-}NPh]_2$ reported in literature.[27]

To confirm the molecular structure of complex **4c**, single-crystal X-ray diffraction analysis was performed with a suitable crystal, which was grown at −35 °C from concentrated *n*-pentane. Complex **4c** crystallized in the orthorhombic space group $Pna2_1$ with eight molecules in the unit cell. Figure 4

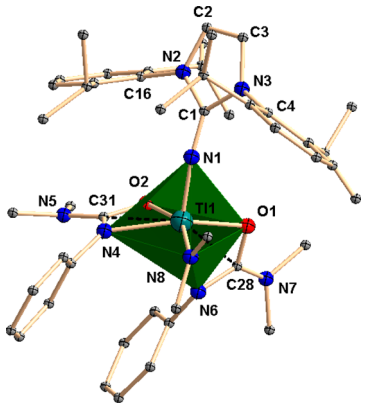
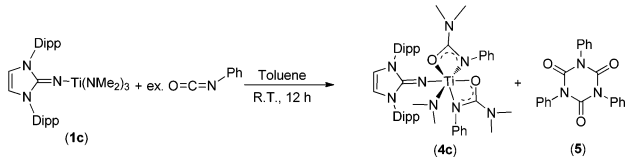


Figure 4. Solid-state structure of complex **4c** showing a distorted octahedral polyhedron around a titanium metal ion. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ti1−N1 1.836(3), Ti1−N4 2.111(3), Ti1−N6 2.302(3), Ti1−N8 1.926(3), Ti1−O1 2.070(2), Ti1−O2 2.168(2), C28−O1 1.288(4), C28−N6 1.337(4), C28−N7 1.352(5), C31−O2 1.288(4), C31−N4 1.353(4), N1−C1 1.288(4), C1−N1−Ti1 160.6(2), N1−Ti1−N4 106.4(1), N1−Ti1−N8 100.8(1), N1−Ti1−N6 155.5(1), O2−Ti1−N4 62.0(1), N1−Ti1−O1 95.4(1), N6−Ti1−N4 92.8(1), N6−Ti1−O1 60.5(9), N6−Ti1−O2 78.3(9), N8−Ti1−O1 107.7(1), N8−Ti1−N6 91.5(1), N8−Ti1−O2 155.7(1).

shows the molecular structure of complex **4c** along with selected bond lengths and bond angles. The solid-state structure of **4c** confirms the ligation of $Im^{Dipp}N^-$, $[OC(=NMe_2)NPh]^-$, and Me_2N^- groups onto the titanium ion.[25,32,33] The geometry around the Ti(IV) center can be best described as distorted octahedral. The coordination sphere of titanium ion consists of one N atom of imidazolin-2-iminato ligand, two N and O atoms coordinated κ^2 fashion from ureate ligands $[(OC(NMe_2)NPh)]$ derived from the insertion of phenyl isocyanates into two of the Ti−NMe_2 bonds of the starting material, along with one remaining −NMe_2 ligand. Coordination of two ureate ligands resulted in the transformation of coordination geometry of titanium from a distorted tetrahedral (in **1c**) to a distorted octahedral (in **4c**). Steric factors may also have dominated migration of the −NMe_2 unit, leading to the trans arrangement of two ureate groups in the complex **4c**. Both the κ^2-$[(OC(NMe_2)NPh)]$ ureate ligands bonded to the titanium ion through one oxygen and one nitrogen atom to yield a planar four-membered ring of sp^2-hybridized N and C centers with an average bite angle of 61.25° (O−Ti−N). The Ti−O bond lengths are different and found to be 2.070(2) Å (Ti1−O1) and 2.168(2) Å (Ti1−O2)—well in agreement with that of reported complexes—2.041(2) Å for $[\sigma{:}\eta^1{:}\eta^5\text{-}(OCH_2)\text{-}(Me_2NCH_2)C_2B_9H_9]Ti[\eta^3\text{-}OC\text{-}(NMe_2)NPh]$[26] and 2.165(3) Å for $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OC\text{-}(NMe_2)\text{-}NPh]_2$.[27] The delocalized π interactions within the OCN moiety (O2−C31−N4 and O1−C28−N6) lead to partial double bond character upon the C−N frame with an average distance of 1.345 Å, whereas O−C bond lengths were 1.288 Å and similar for both the ligands. The Ti−$N_{iminato}$ bond distance [1.836(3) Å] is similar with that in **1c** (1.853(2) Å), and the bond angle of iminato nitrogen at 160.6(2)° (C1−N3−Ti1) is narrower than that of starting material **1c** (169.2(1)°), could be due to higher steric congestion around the titanium ion in **4c** as compared to **1c**.

We observed that, even in the presence of excess carbidiimides and higher reaction temperature, carbodiimides underwent monoinsertion only into the Ti−N σ−bond. The formation of bis-inserted product **4c** with the reaction of isocyanate clearly indicates that the enhanced reactivity of PhNCO is because of the greater electrophilic character of allenic carbon. Further, reaction of excess isocyanate with complex **1c** resulted in the stable bis-inserted product **4c** along with trimer product 1,3,5-trisphenyl-1,3,5-triazinane-2,4,6-trione $(PhNCO)_3$ (**5**), which was isolated and characterized by NMR spectroscopy. Spectra of product **5** were compared to the reported values.[28] Thus, the formation of compound **5** suggests that the third equivalent of isocyanate was unable to undergo further insertion into the Ti−N σ-bond, and it instead reacted with $[(Im^{Dipp}N)Ti[\kappa^2\text{-}OC(NMe_2)NPh]_2(NMe_2)]$ moiety to result in the formation of cyclic trimer $(PhNCO)_3$ (**5**), presumably due to steric crowding around the titanium ion (Scheme 4). Xie and co-workers have already reported[27] the

Scheme 4. Reaction of Complex 1c with Excess Phenyl Isocyanate



reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ with excess of phenyl isocyanate thus affording formation of the same cyclic trimer **5**. Similar trimarization processes are also reported with lanthanide complexes[29] and titanium complexes.[30]

Preparation and Structural Characterization of Titanium Tris(thioureate) Complex $[(Im^{Dipp}N)Ti\{\kappa^2\text{-}SC(NMe_2)\text{-}NPh\}_2\{\kappa^1\text{-}SC(NMe_2)NPh\}]$ (6c). We observed the diverse reactivity of imidazolin-2-iminato titanium complex with various heteroallene molecules. In those reactions, Ti−N_{amide} bond was monoinserted into RN═C═NR and bis-inserted into PhN═C═O framework leading to the corresponding guanidinate and ureate complexes, respectively. It was further observed that excess equivalent of hetero allene moiety did not react with the Ti−$N_{iminato}$ bond. To get a better insight into the insertion reactions with polar allene, we performed a reaction of **1c** with 3 equiv of phenyl isothiocyanate (PhNCS) in toluene solution and at ambient temperature. The tris-insertion product $[(Im^{Dipp}N)Ti\{\kappa^2\text{-}SC(NMe_2)NPh\}_2\{\kappa^1\text{-}SC(NMe_2)NPh\}]$ (**6c**) was obtained in 54% yield (Scheme 5). It was noted that the controlled reaction to isolate mono- or bis-inserted product led to the formation of the complex **6c** in each case.

The complex **6c** was characterized by standard NMR spectroscopy and combustion analysis, and its solid-state structure was established by single-crystal X-ray analysis. ^1H NMR spectra measured in C_6D_6 showed characteristic peaks at δ 1.21 and 1.18 ppm for diastereotopic methyl protons of isopropyl groups with coupling constant of 6.86 Hz each, whereas methine protons of isopropyl groups appeared at δ

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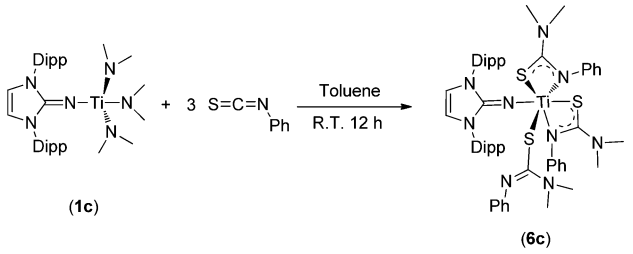
Scheme 5. Synthesis of Complex 6c from 1c



3.29 ppm as broad septets. The olefinic protons of the imidazolin-2-iminato ligand backbone resonated at δ 5.83 ppm, which was slightly shifted upfield to that of complex **1c** (5.92 ppm). Aromatic protons of three phenyl rings resonated at δ 7.37−7.20 ppm. The $^{13}C\{^1H\}$ NMR spectra gave crucial information—two resonance peaks at δ 151.2 and 150.8 ppm were observed by us—these can be assigned to the two thioureate carbons (NCS), and the values are slightly upfield shifted to that (174.91 ppm) of complex reported by Xie and co-workers $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)[\eta^2\text{-}SC(NMe_2)N^nBu]$.[27] Two distinct resonating signals for SCN carbon appeared due to the different electronic environments of ambidentate thioureate ligand, which showed both κ^2 and κ^1 coordination modes. The *ipso*-carbon of phenyl ring appeared at δ 147.5, 147.0, and 134.8 ppm.

The solid-state structure of complex **6c** (shown in Figure 5) confirmed the attachment of thioureate fragment to titanium metal through two different coordination modes. Two thioureate ligand moieties coordinated to the titanium metal ion in κ^2-mode through sulfur and nitrogen atoms, while the third thioureate ligand coordinated through the sulfur atom in a κ^1-mode. The reason why sulfur was preferred over nitrogen to coordinate to the titanium ion in the latter case was that steric hindrance around the titanium metal center did not allow the third thioureate ligand to coordinate in κ^2-mode. Two four-membered metallacycles (S3−C46−N8−Ti1 and S2−C37−N6−Ti1) were formed by the chelating of two thioureate building blocks having an average bite angle of (S−Ti−N) 65.68°. The Ti−S bond distance observed for κ^1-(SC(NMe$_2$)-NPh) moiety [Ti1−S1 2.393(7) Å] was much shorter than that present in κ^2-(SC(NMe$_2$)NPh) moieties (Ti1−S2) 2.464(7) and (Ti1−S3) 2.516(7) Å due to greater accumulation of negative charge over sulfur atom in κ^1-(SC(NMe$_2$)NPh) moiety, thus indicating that S1 is bonded to titanium ion by σ-bonding, whereas S2 and S3 present in κ^2-(SC(NMe$_2$)NPh) moieties were participating in delocalization of electronic charge through SCN skeletons. The delocalized π interactions within the SCN moiety (S2−C37−N6 and S3−C46−N8) led to partial double bonded C−N distances [C37−N7 1.362(3) Å and C46−N9 1.357(3) Å], whereas the S−C bond lengths were similar for both the ligands. The S2−C37 and S3−C46 bond lengths [1.748(3) and 1.728(3) Å] are slightly shorter than that of S1−C28 1.790(2) Å, thereby indicating that S1−C28 is purely of single-bond character.

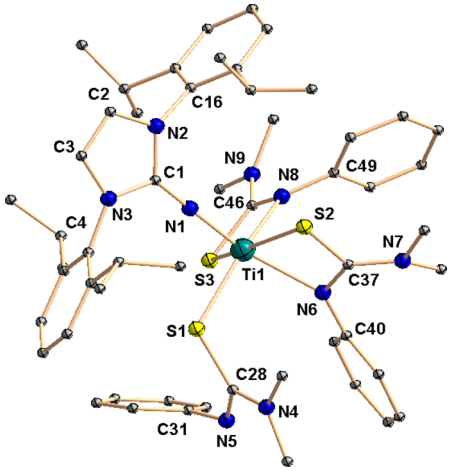


Figure 5. Solid-state structure of complex **6c**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ti1−N1 1.800(2), N1¬−C1 1.304(3), Ti1−S1 2.393(7), Ti1−S2 2.464(7), Ti1−S3 2.516(7), Ti1−N8 2.180(2), Ti1−N6 2.250(2), S3−C46 1.728(3), N8−C46 1.325(3), C46−N9 1.357(3), S1−C28 1.790(2), N5−C28 1.290(3), N4−C28 1.368(3), S2−C37 1.748(3), C37−N6 1.318(3), N7−C37 1.362(3), Ti1−N1−C1 170.3(2), N1−Ti1−S1 90.5(6), N1−Ti1−N6 157.2(8), N1−Ti1−N8 102.7(8), N1−Ti1−S2 91.8(6), N1−Ti1−S3 100.3(6), S3−Ti1−S2 158.9(3), S1−Ti1−S3 92.4(3), S3−Ti1−N8 65.7(5), S2−Ti1−N6 92.3(5), S2−Ti1−N8 94.8(5), S3−Ti1−N6 102.2(5), S1−Ti1−S2 104.9(3), S2−C37−N6 112.5(2), S2−C37−N7 120.2(2), N6−C37−N7 127.2(2), S3−C46−N8 113.5(2), S3−C46−N9 121.6(2), N8−C46−N9 124.9(2), S1−C28−N5 125.2(2), S1−C28−N4 116.8(2), N4−C28−N5 117.8(2).

The complex **6c** is a rare example in which the hard titanium metal center is preferred to coordinate a soft sulfur atom instead of a hard nitrogen donor from the thioureate scaffold to achieve a lesser crowding arrangement around the metal center, as the coordination through nitrogen could lead to much more steric crowding onto the metal ion.

Catalytic Addition of N−H Bond to Isocyanates in the Presence of Precatalyst Complex 1c. In the stoichiometric reaction of **1** with various heterocumelenes like carbodiimide, phenyl isocyanate, and phenyl isothiocyanate, we observed that carbodiimides underwent monoinsertion, whereas isocyanate yielded bis-insertion, while isothiocyanate afforded tris-insertion into the Ti−N$_{amido}$ bond of complex **1**. From these results we can envisage that titanium complex **1** can be used as a precatalyst for the preparation of guanidine and urea derivative by the reaction of either carbodiimides or isocyanates with various amines through insertion reactions. Using a similar approach, Tamm and Eisen recently demonstrated the catalytic addition of E−H bonds (E = N, P, S) to carbodiimides, isocyanates, and isothiocyanates using thorium complex $[Th(Im^{Dipp}N)\{N(SiMe_3)_2\}_3]$.[16]

In this study, we described the catalytic addition of N−H bonds from various amines to phenyl isocyanate and carbodiimides with complex **1c** as the precatalyst. Catalytic experiments were performed using 5 mol % of titanium complex $[Im^{Dipp}NTi(NMe_2)_3]$ (**1c**) and equimolar amounts of either isocyanate or carbodiimides and amines, which were added to a toluene solution of the catalyst under an inert atmosphere (Scheme 6).

The reaction mixture in each case was kept under stirring either at room temperature or elevated temperature (60 °C for entry 2) for 12 h, and the respective urea or guanidine products were isolated. The isolated products were analyzed through ^1H and ^{13}C NMR spectroscopy, and yields were calculated after isolation of pure products (Table 1). The reaction of phenyl isocyanate with aromatic amines like 2,6-diisopropylaniline mesityl amine and 2,6-dimethylamine afforded the respective urea derivative in high yield (entries 1−3). However, the reactions with 1-fluoroaniline were sluggish, as only low yield of

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Scheme 6. Catalytic Formation of Urea and Guanidine Derivatives Using 1c as Precatalyst

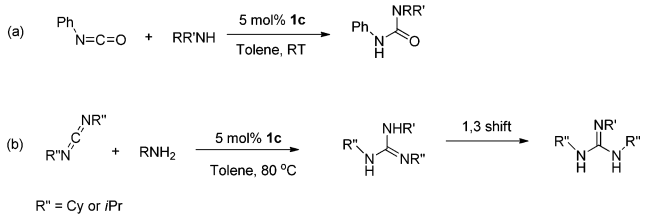
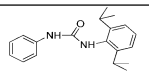
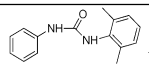
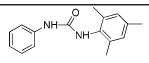
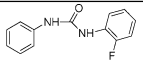
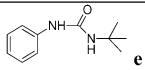
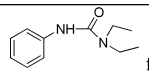
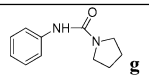
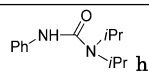
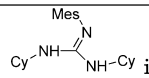
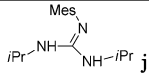


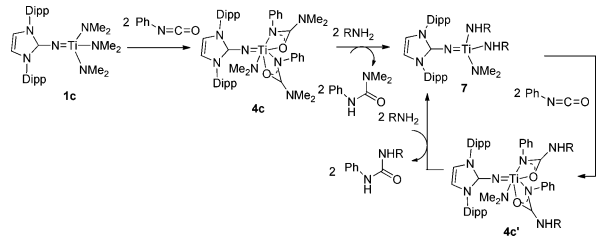
Table 1. Catalytic Reactions of Isocyanates with $ArNH_2$ Using 1c as Precatalyst[a]

Entry	Isocyanate/carbodiimde	$ArNH_2$	Products	Yield [%][b]
1	PhNCO	$DippNH_2$	 **a**	97
2	PhNCO	2,6-$Me_2C_6H_3NH_2$	 **b**	88
3	PhNCO	$MesNH_2$	 **c**	93
4	PhNCO	*o*-F-$C_6H_4NH_2$	 **d**	54
5	PhNCO	*tert*-butylamine	 **e**	85
6	PhNCO	Et_2NH	 **f**	74
7	PhNCO	Pyrrolidine	 **g**	85
8	PhNCO	N,N Diisopropylethylamine	 **h**	62
9	CyNCNCy	$MesNH_2$	 **i**	trace
10	*i*PrN-CN*i*Pr	$MesNH_2$	 **j**	trace

[a]All reactions were performed in toluene solvent; reaction time 12 h at room temperature (60 °C for entry 2); compounds were isolated and purified by washing with *n*-pentane. All compounds were characterized by NMR spectroscopy using C_6D_6 for compounds **a**–**d**, whereas $CDCl_3$ for compounds **e**–**h** as solvent. [b]Yields are calculated from isolated pure products.

the respective urea derivatives as products were observed (entry 4) under similar conditions. While the conversion of the aliphatic primary amines (entry 5) was quite good, the secondary amines (entry 6 and 7) were converted to their respective inserted product in much higher yield presumably due to positive inductive effect of the alkyl groups attached to the nitrogen atom. In contrast, the conversions of carbodiimides (*N*,*N*′-dicyclohexyl or *N*,*N*′-diisopropyl) to yield the corresponding guanidine were not observed (entries 5 and 6) even after prolonged reaction times and heating to 80 °C. Thus, the scope of catalytic addition of the N–H bonds by using imidazolin-2-iminato titanium complex **1c** as catalyst was limited to the phenylisocyanate.

Scheme 7. Most Plausible Mechanism for the Catalytic Addition of N–H Bond to Isocyanate by Titanium Precatalyst 1c

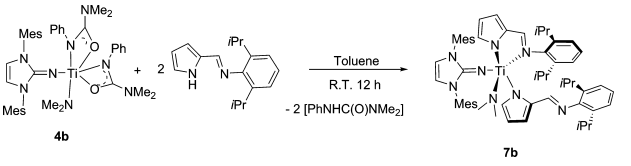


The most plausible mechanism for the catalytic addition of N–H bond to isocyanate by the titanium precatalyst **1c** is shown in Scheme 6. Similar mechanistic cycles were also demonstrated recently by Tamm and Eisen using [Th(Im^{Dipp}N){N(SiMe$_3$)$_2$}$_3$] complex as precatalyst.[16] The stoichiometric reaction between PhN=C=O and the complex **1c** led to the formation of titanium complex **4c** whose molecular structure was already established. This indicated that nucleophilic attack by the titanium bound -NMe_2 group to generate complex **4c** occurred at the phenyl isocyanate carbon center in the initiation step. In the next step, complex **4c** reacted with 2 equiv of amines to give the corresponding titanium amido complex **7**, which was converted to ureate complex **4c**′, analogous to **4c**, by the reaction of 2 equiv of phenyl isocyanate. In the final step to propagate the catalytic cycle (Scheme 6), complex **4c**′ reacted with another 2 equiv of amine to yield the product urea and the active catalyst **7**.

To get more insight about the mechanistic cycle, we performed a stoichiometric reaction of **4b** and freshly distilled 2,6-diisopropylaniline in toluene at ambient temperature to isolate the titanium amido complex **7a**. The resulting compound was dried under vacuum. Several attempts to crystallize the compound were not successful, and the NMR spectrum of the crude compound is presented in Supporting Information (FS 13). The spectral data of the crude compound indicated the formation of complex **7a** along with the corresponding urea derivative.

However, the formation of the active catalyst was confirmed by isolating the titanium complex **7b** prepared by the stoichiometric reaction of complex **4b** in toluene solution at ambient temperature (Scheme 8). We chose the iminopyrole ligand as an amine source due to its bulky nature and potential bidentate coordination mode, which could stabilize the corresponding intermediate titanium complex.

Scheme 8. Synthesis of Active Catalyst 7b from Complex 4b



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Complex **7b** was characterized using spectroscopic and analytical methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded in benzene-d_6. ^{1}H NMR spectra showed two sharp resonance peaks at 7.92 and 7.75 ppm, which could be assigned to the imine proton of two different iminopyrrolyl ligands coordinated in κ^1 and κ^2 mode. The molecular structure of complex **7b**, as shown in Figure 6, was confirmed by single-crystal X-ray diffraction analysis.

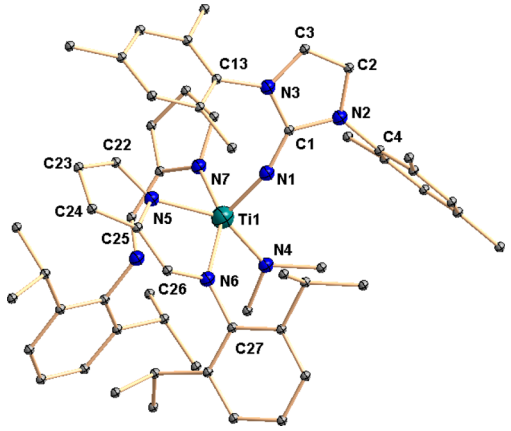

Figure 6. Molecular structure of complex **7b**. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ti1−N1 1.806(2), Ti1−N4 1.916(2), Ti1−N5 2.139 (2), Ti1−N6 2.266(2), Ti1−N7 2.119(2), N1−C1 1.309(3), C42−N7 1.386(3), C43−N8 1.283(3), N5−C25 1.386(3), C26−N6 1.309(3), C1−N1−Ti1 160.0(1), N1−Ti1−N4 103.4(8), N1−Ti1−N5 103.6(7), N1−Ti1−N6 107.0(7), N1−Ti1−N7 94.9(7), N6¬−Ti1−N7 152.1(7), N5¬−Ti1−N7 84.8(7), N4−Ti1−N5 150.3(7).

Complex **7b** crystallized in the triclinic space group $P\bar{1}$, with two molecules in the unit cell along with two molecules of toluene as solvent. The coordination polyhedron in complex **7b** was formed by the coordination with one imidazolin-2-iminato nitrogen atom, two pyrrolide, and one imine nitrogen atom from two iminopyrrolyl ligands, and one nitrogen atom from the dimethylamide group. The overall geometry of the central titanium ion can be described as a distorted square pyramidal with the imido nitrogen N1 atom positioned at the axial position and the other four nitrogen atoms, N4, N5, N6, and N7, forming the basal plane of the square pyramid. The Ti−$N_{iminato}$ bond distance [1.806(2) Å] for **7b** was within the values obtained for **4c** [1.836(3) Å]. Further, the Ti1−N1−C1 angles [160.0(1)° for **7b** vs 160.6(2) for **4c**] indicate a stronger coordination of the imidazolin-2-iminato nitrogen to the titanium ion. From the molecular structure we could observe that one iminopyrrolide ligand was bonded in κ^2 mode, whereas the second iminopyrrolide ligand was coordinated to the titanium atom through κ^1 mode. However, such differentiation in coordination modes can presumably be due to the smaller ionic radius of the titanium ion and sterically larger size of the ligands. The bond distances of Ti−N_{pyr} [Ti1−N5 2.139(2) Å; Ti1−N7, 2.119(2) Å] were shorter than those of Ti1−N_{imine} [Ti1−N6, 2.266(2) Å] and are in the range reported in the literature.[31]

SUMMARY

With this contribution, we have demonstrated the synthesis and molecular structures of three different (mono) imidazolin-2-iminato titanium dimethylamide complexes (**1a−c**). A very short Ti−N bond in all the complexes was observed to manifest the strong electron donation from the imidazolin-2-iminato fragment to the titanium ion. In the stoichiometric reaction of **1** with carbodiimides, monoinsertion of the RNCNR to the Ti−N_{amide} occurred. However, the reactions with isocyanate and isothiocyanate with **1** under a similar condition yielded bis- and tris-inserted products, respectively, indicating the enhanced electrophilicity of the heterocumelene carbon center in isocyanate and isothiocyanate rather than that in carbodiimides. We have also demonstrated the scope of the catalytic addition of the N−H bonds of various amines with phenyl isocyanate and carbodiimides (DCC or DIC) by using imidazolin-2-iminato titanium complex **1c**, and observed that while a smooth conversion of the amines with isocyanate occurred, no conversion was observed with carbodiimides under similar reaction conditions. In addition, we have established the mechanism of the catalytic reaction confirming the molecular structure of the active catalyst **7b**.

EXPERIMENTAL SECTION

General Consideration. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line interfaced with a high-vacuum (1×10^{-4} Torr) line or in an argon-filled M. Braun glovebox. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glovebox. Dichloromethane was freshly distilled under CaH_2 and stored under molecular sieves. ^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (100 MHz) spectra were recorded on a Bruker Avance III-400 spectrometer. A Bruker Alpha FT-IR was used for the FT-IR measurements. Elemental analyses were performed on a Bruker Euro EA at the Indian Institute of Technology Hyderabad. Imidazolin-2-imines Im^RNH (R = *t*Bu, Mes, Dipp) and *N*-aryliminopyrrolyl (ImpDipp) were prepared according to the published procedures.[17] $Ti(NMe_2)_4$, carbodiimides, *tert*-butylamine, 2,6-diisopropylaniline, and mesityl amine were purchased from Alfa Aesar and used as received. The NMR solvents $CDCl_3$ and C_6D_6 were purchased from Sigma-Aldrich and dried by either molecular sieve ($CDCl_3$) or a Na/K alloy (C_6D_6) prior to use. ***Caution!*** *Phenyl isocyanate and phenyl isothiocyanate are very hazardous substances.*

General Procedure for the Preparation of Imidazolin-2-iminato Titanium Amido Complexes [$(Im^RN)Ti(NMe_2)_3$] [R = *t*Bu, (1a); Mes, (1b) and Dipp, (1c)]. In a 25 mL dry Schlenk flak, respective imidazoline-2-imine [Im^RNH; R = *t*Bu (196 mg), R = Mes (320 mg), and R = Dipp (404 mg)] was placed, and 5 mL of dry toluene was added to it. To this solution, a mixture of tetrakis-(dimethylamino)titanium (225 mg) and 5 mL of toluene was also added. The solution immediately turned red, and resulting mixture was heated to 90 °C for 12 h and kept under stirring condition. The solvent was evaporated under vacuo to obtain a red colored solid, which was recrystallized as yellow crystals from *n*-pentane at −35 °C. Compounds **1a−c** are soluble in THF, *n*-pentane, *n*-hexane, and toluene.

Analytical Data for [$(Im^{tBu}N)Ti(NMe_2)_3$]) (1a). Yield: 448 mg (95%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 5.95 (s, 2H, NC*H*), 3.37 (s, 18H, $N(CH_3)_2$), 1.58 (s, 18H, $C(CH_3)_3$) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, 25 °C): 141.2 (*N*CN), 106.9 (NCH=CHN) 55.6 ($C(CH_3)_3$), 45.8 ($N(CH_3)_2$), 28.0 ($C(CH_3)_3$). Elemental analysis calculated (%) for $C_{45}H_{97}N_{15}Ti_2$ (944.1; 2x**1a**.$Im^{tBu}NH$): C 57.25, H 10.36, N 22.25; found C 56.89, H 9.93, N 21.83.

Analytical Data for [$(Im^{Mes}N)Ti(NMe_2)_3$]) (1b). Yield: 437 mg (88%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.80 (s, 4H, *m*-Ph), 5.68 (s, 2H, NC*H*), 3.01 (s, 18H, $N(CH_3)_2$), 2.25 (*o-attached* CH_3), 2.13 (*p-attached* CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, 25 °C): 152.0 (*ipso*-phenyl), 138.6 (*N*CN), 137.0 (*o*-phenyl), 134.9 (*p*-phenyl), 128.9 (*m*-phenyl), 111.7 (NCH=CHN), 38.9 (NCH_3), 21.2 (*p-attached* CH_3), 18.6 (*o-attached* CH_3). Elemental analysis

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calculated (%) for $C_{27}H_{42}N_6Ti$ (498.5): C 65.05, H 8.49, N 16.86; found C 64.72, H 8.19, N 16.41.

Analytical Data for [($Im^{Dipp}N$)Ti(NMe_2)$_3$]) (1c). Yield: 525 mg (90%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.34−7.17 (m, 4H, Ar), 7.15−7.10 (m, 2H, Ar), 5.92 (s, 2H, NC*H*), 3.24 (sept, 4H, C*H*(CH_3)$_2$, 2.91 (s, 18H, N(CH_3)$_2$), 1.41 (d, 12H, J = 6.85 Hz, CH(CH_3)$_2$), 1.20 (d, 12H, J = 6.85 Hz, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 147.9 (*ipso*-phenyl), 141.5 (NCN), 135.3 (*o*-phenyl), 129.3 (*p*-phenyl), 124.1 (*m*-phenyl), 113.8 (NCH═*C*HN), 45.1 (NCH_3), 29.0 (CHCH_3), 24.6 (CHCH_3), 23.4 (*C*HCH_3). Elemental analysis calculated (%) for $C_{33}H_{54}N_6Ti$ (582.7): C 68.02, H 9.34, N 14.42; found C 67.79, H 8.87, N 14.07.

General Procedure for the Preparation of Imidazolin-2-iminato Titanium Mono(guanidinate) Complexes [(Im^RN)Ti(R′NC(NMe_2)NR′)(NMe_2)$_2$] (R = *t*Bu; R′ = *i*Pr (2a), R = Dipp; R′ = *i*Pr (2c); R = *t*Bu; R′ = Cy (3a)). In a 25 mL dry Schlenk flask, compound **1** (0.267 mmol) was placed, and a solution of respective carbodiimides (0.267 mmol) and 5 mL of toluene was added on to it. The reaction mixture was kept heated to 90 °C and kept under stirring condition for 6 h. The solvent was evaporated under vacuo to obtain a red residue, which was washed with *n*-pentane (2 × 5 mL). The title compound was recrystallized from toluene at −35 °C.

Analytical Data for [(Im^{tBu}N)Ti(*i*PrNC(NMe_2)-N*i*Pr) (NMe_2)$_2$] (2a). Yield: 113 mg, 85%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 5.85 (s, 2H, NC*H*), 3.51−3.58 (m, 2H, C*H*(CH_3)$_2$), 3.39 (s, 12H, N(CH_3)$_2$), 2.53 (s, 6H, N(CH_3)$_2$), 1.58 (s, 18H, C(CH_3)$_3$) 1.12 (d, 12H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 153.2 (NCN), 141.9 (NCN), 107.3 (NCH═CHN) 57.4 (N(CH_3)$_2$), 55.6 (*C*(CH_3)$_3$), 45.8 (N(CH_3)$_2$), 28.0 (C(*C*H$_3$)$_3$) ppm. FT-IR (selected frequencies): ν = 2922 (s), 2843 (s), 2753 (s), 1636 (m), 1512 (s), 1442 (m), 1389 (m), 1164 (s), 943 (s), 801 (s), 550 (s) cm^{-1}. Elemental analysis: $C_{24}H_{52}N_8Ti$ (500.38): Calcd (%) C 57.58, H 10.47, N 22.38. Found C 57.31, H 10.24, N 21.98.

Analytical Data for [(Im^{Dipp}N)Ti(*i*PrNC(NMe_2)-N*i*Pr) (NMe_2)$_2$] (2c). Red crystals were obtained after 2 d. Yield: 151 mg, 80%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.20−7.15 (m, 6H, Ar), 5.95 (s, 2H, NC*H*), 3.71−3.76 (m, 2H, C*H*(CH_3)$_2$), 3.46 (m, 4H, C*H*(CH_3)$_2$), 2.88 (s, 12H, N(CH_3)$_2$), 2.50 (s, 6H, N(CH_3)$_2$), 1.14 (d, 12H, $^3J_{HH}$ = 6.80 Hz, CH(CH_3)$_2$), 1.12 (br, 12H, CH(CH_3)$_2$), 1.16 (d, 12H, $^3J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 153.2 (NCN), 150.1 (*ipso*-phenyl), 138.2 (NCN), 135.3 (*o*-phenyl), 130.2 (*m*-phenyl) 126.0 (*p*-phenyl), 116.3 (NCH═CHN) 49.4 (N(CH_3)$_2$), 45.8 (N(CH_3)$_2$), 29.0 (CH(CH_3)$_2$), 24.6 (CH(CH_3)$_2$), 23.4 (CH(CH_3)$_2$) ppm. Elemental analysis: $C_{40}H_{68}N_8Ti$ (706.85): Calcd (%) C 67.77, H 9.67, N 15.81; Found C 67.34, H 9.26, N 15.21.

Analytical Data for [(Im^{tBu}N)Ti(CyNC(NMe_2)-NCy)(NMe_2)$_2$] (3a). Yield 106 mg, 68%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 5.90 (s, 2H, NC*H*), 3.58 (s, 12H, N(CH_3)$_2$), 3.22−3.19 (m, 2H, Cy), 2.64 (s, 6H, N(CH_3)$_2$), 1.88−1.85 (m, 10H, Cy), 1.60 (s, 18H, C(CH_3)$_3$), 1.28−1.24 (m, 10H, Cy) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 169.6 (NCN), 138.4 (NCN), 106.6 (NCH═CHN) 57.4 (N(CH_3)$_2$), 55.6 (*C*(CH_3)$_3$), 50.0 (N(CH_3)$_2$), 40.4 (Cy), 35.9 (Cy), 29.0 (C(CH_3)$_3$), 27.0 (Cy), 26.5 (Cy) ppm. FT-IR (selected frequencies): ν = 3234 (w), 2929 (w), 2843 (w), 2279 (s), 1619 (m), 1585 (s), 1452 (m), 1329 (m), 1112 (s), 811 (s) cm^{-1}. Elemental analysis: $C_{30}H_{60}N_8Ti$ (580.73): Calcd (%) C 62.05, H 10.41, N 19.30. Found C 61.88, H 10.37, N 19.21.

Preparation of Imidazolin-2-iminato Titanium Bis(ureate) Complex [(Im^RN)Ti{κ^2-OC(NMe_2)NPh}$_2$(NMe_2)] (4b, R = Mes, 4c, R = Dipp). A solution of **1b** (200 mg, 0.401 mmol) or **1c** (200 mg, 0.343 mmol) in toluene (6 mL) was added to a solution of phenyl isocyanate (95.53 mg, 0.802 mmol for **4b**) and (81.71 mg, 0.686 mmol for **4c**) in toluene (8 mL). An immediate dark red colored solution was formed. Resulting reaction mixture was stirred for 6 h at ambient temperature. The solvent was evaporated under vacuo, and the compound was extracted from 15 mL of *n*-pentane. The compound **4c** was recrystallized from 3 mL of *n*-pentane.

Analytical Data for [(Im^{Mes}N)Ti(κ^2-OC(NMe_2)-NPh)$_2$(NMe_2)] (4b). Yield: 222 mg, 75%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.09−7.15 (m, 10H, Ph), 6.81 (s, 4H, Ar), 5.65 (s, 2H, NC*H*), 3.33 (s, 6H, N(CH_3)$_2$), 2.37 (s, 6H, CH_3), 2.33 (s, 12H, CH_3), 2.10 (s, N(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 150.5 (OCN), 148.3 (*ipso*-Ar), 141.5 (NCN), 137.8 (*o*-phenyl), 137.2 (*p*-Ar), 134.2 (*ipso*-Ar), 129.0 (*m*-Ar), 127.8 (*o*-Ph), 127.4 (*m*-Ph), 120.7 (*p*-Ph), 112.5 (NCH═CHN), 51.3 (N(CH_3)$_2$), 37.5 (N(CH_3)$_2$), 21.2 (*o-attached* CH_3), 18.3 (*p-attached* CH_3) ppm. Elemental analysis: $C_{41}H_{51}N_8O_2Ti$ (736.8): Calcd (%) C 66.84, H 7.11, N 15.21. Found C 66.59, H 6.93, N 14.88.

Analytical Data for [(Im^{Dipp}N)Ti(κ^2-OC(NMe_2)-NPh)$_2$(NMe_2)] (4c). Yield: 197 mg, 70%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.23−7.17 (m, 2H, Ar), 7.15−7.10 (m, 10H, Ph), 6.86−6.80 (m, 4H, Ar), 5.87 (s, 2H, NC*H*), 3.39 (sept, 4H, $^3J_{HH}$ = 6.80 Hz C*H*(CH_3)$_2$, 3.13 (s, 6H, N(CH_3)$_2$), 1.56 (s, 12H, N(CH_3)$_2$), 1.25 (d, 24H, $^3J_{HH}$ = 6.85 Hz, CH(CH_3)$_2$), 1.20 (d, 12H, $^3J_{HH}$ = 6.88 Hz, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 149.2 (OCN), 147.9 (*ipso*-phenyl), 141.5 (NCN), 138.6 (*o*-phenyl), 134.9 (*ipso*-Ph), 129.3 (*m*-phenyl), 127.9 (Ph), 123.7 (*p*-phenyl), 114.3 (NCH═CHN), 51.6 (N(CH_3)$_2$), 37.4 (N(CH_3)$_2$), 29.0 (CHCH$_3$), 24.8 (CH(CH_3)$_2$), 23.7 (CH(CH_3)$_2$) ppm. FT-IR (selected frequencies): ν = 3298 (s), 2957 (s), 2865 (s), 1640 (s), 1530 (s), 1471 (m), 1370 (m), 1247 (s), 1059 (w), 805 (s), 753 (s), 603 (m) cm^{-1}. Elemental analysis: $C_{47}H_{64}N_8O_2Ti$ (820.46): Calcd (%) C 68.76, H 7.86, N 13.65. Found C 67.92, H 7.57, N 13.23.

Preparation of of 1,3,5-trisphenyl-1,3,5-triazinane-2,4,6-trione (5). A solution of **1c** (200 mg, 0.343 mmol) in toluene (6 mL) was added to a solution of phenyl isocyanate (245.13 mg, 2.058 mmol) in toluene (15 mL). The reaction mixture was kept under stirring at room temperature for 6 h. Solvent was evaporated under vacuo, and the compound was extracted in *n*-pentane (20 mL) and kept for crystallization after reducing the solvent volume to 4 mL. Red colored crystals were obtained after 12 h, and the crystals that were separated from mother liquor and characterized by X-ray crystallography were identified as complex **4c**. From same mother liquor colorless crystals obtained after 24 h were characterized by NMR spectroscopy and identified as compound **5**. Yield: 0.105 g, 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.40 ppm. (m, 15H, Ar); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.4, 133.2, 129.1, 128.0 ppm. Elemental analysis: $C_{21}H_{15}N_3O_3$ (357.36): Calcd (%) C 70.58, H 4.23, N 11.76. Found C 70.24, H 4.65, N 11.12.

Preparation of Imidazolin-2-iminato Titanium Tris(thioureate) Complex [(Im^{Dipp}N)Ti{κ^2-SC(NMe_2)NPh}$_2${κ^1-SC(NMe_2)NPh}] (6c). A solution of **2c** (200 mg, 0.343 mmol) in toluene (6 mL) was added to a solution of phenyl isothiocyanate (139.11 mg, 1.029 mmol) in toluene (8 mL), which resulted an immediate formation of dark red solution. The resulting reaction mixture was stirred for another 6 h at ambient temperature. The solvent was evaporated under vacuo, and the compound was extracted from 15 mL of *n*-pentane. The title compound was recrystallized from 3 mL of *n*-pentane at −35 °C. Yield: 0.183 g, 54%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.37−7.20 (m, 15H, Ph), 7.03−6.98 (4H, Ar), 6.82−6.76 (m, 2H, Ar), 5.83 (s, 2H, NC*H*), 3.28 (sept, 4H, $^3J_{HH}$ = 6.84 Hz C*H*(CH_3)$_2$), 3.4 (s, 6H, N(CH_3)$_2$), 2.38 (s, 12H, N(CH_3)$_2$), 1.21 (d, 24H, $^3J_{HH}$ = 6.85 Hz, CH(CH_3)$_2$), 1.18 (d, 12H, $^3J_{HH}$ = 6.84 Hz, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 151.2 (SCN), 150.8 (SCN), 147.8 (*ipso*-phenyl), 147.5 (*ipso*-phenyl), 147.0 (*ipso*-Ph), 137.8 (*o*-phenyl), 134.8 (*ipso*-Ph), 130.1 (*m*-phenyl), 129.4 (Ar), 127.9 (Ph), 127.1 (Ph), 124.7 (*p*-phenyl), 124.5 (*p*-phenyl), 123.4 (Ar), 121.8 (Ar), 120 (Ar), 114.6 (NCH═CHN), 51.6 (N(CH_3)$_2$), 40.6 (N(CH_3)$_2$), 40.5 (N(CH_3)$_2$), 25.4 (CH(CH_3)$_2$), 25.1 (CH(CH_3)$_2$), 23.3 (CH(CH_3)$_2$) ppm. Elemental analysis: $C_{54}H_{69}N_9S_3Ti$ (988.25): Calcd (%) C 65.63, H 7.04, N 12.76. Found C 65.26, H 6.84, N 12.69.

Preparation of [(Im^{Mes}N)Ti{2-(2,6-*i*Pr$_2$$C_6H_3$N═CH)-$C_4H_3$N}$_2$($NMe_2$)$_2$] (7b). In a flame-dried 25 mL Schlenk flask compound **4b** [prepared from 200 mg, 0.401 mmol **1b** and phenyl isocyanate (96 mg, 0.806 mmol) analogous to **4c**] and 5 mL of toluene was taken. To this solution, (2,6-diisopropylphenyl)[(1*H*-pyrrol-2-yl)methylene]-amine (204.1 mg, 0.804 mmol) was added along with 5 mL of toluene. The resulting reaction mixture was kept under stirring for 12 h at room temperature. The solvent was evaporated under vacuo, and

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red color solid was obtained, which was dissolved in toluene (10 mL) and filtered off. The filtrate was concentrated to 3 mL and was stored at −35 °C. Red colored crystals were obtained after 2 d. Yield: 0.240 g, 65%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.92 (s, 1H, N=C*H*), 7.75 (s, 1H, N=C*H*), 7.64 (s, 2H, 5-pyr), 7.15−7.11 (m, 6H, Ar), 7.09−7.04 (m, 4H, Ar), 7.02−7.00 (m, 2H, 3-pyr), 6.67−6.50 (m, 2H, 4-pyr), 5.45 (s, 2H, NC*H*), 3.16 (sept, 2H, $^3J_{HH}$ = 6.84 Hz, C*H*$(CH_3)_2$), 3.08−2.95 (m, 2H, C*H*$(CH_3)_2$), 2.83 (s, 12H, N$(CH_3)_2$), 2.11 (s, 12H, CH_3), 2.04 (s, 6H, CH_3), 1.17 (d, 12H, $^3J_{HH}$ = 6.84 Hz, CH$(CH_3)_2$), 1.03 (d, 12H, $^3J_{HH}$ = 6.36 Hz, CH$(CH_3)_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): 162.4 (N=CH), 165.4 (N=CH), 152.0 (*ipso*-C_6H_3), 139.0 (*ipso*-C_6H_3), 137.8 (NCN), 130.0 (2-pyr), 125.7 (3-pyr), 123.3 (*o*-C_6H_3), 126.0 (*p*-C_6H_3), 123.2 (*m*-C_6H_3), 118.1 (4-pyr), 110.2 (5-pyr), 107.2 (NCH=CHN), 50.2 (N$(CH_3)_2$), 28.3 (C$(CH_3)_3$), 27.8 (CH$(CH_3)_2$), 27.2 (CH$(CH_3)_2$), 22.8 (CH$(CH_3)_2$) 21.4 (CH_3), 21.0 (CH_3) ppm. Elemental analysis: $C_{64}H_{80}N_8Ti$ (988.25): Calcd (%) C 76.16, H 7.99, N 11.10. Found C 75.89, H 7.52, N 10.68.

General Procedure for the Catalytic Addition of Amines with Carbodiimide or Phenyl Isocyanate. A solution of primary or secondary amine (0.8394 mmol) in toluene (1.0 mL) was added dropwise into the reaction mixture of phenyl isocyanate (0.8394 mmol) and [(Im^{Dipp}N)Ti$(NMe_2)_3$] (0.042 mmol) to a 25 mL dry Schlenk flask inside the glovebox. The dark red reaction mixture was stirred for 12 h at room temperature. Solvent was evaporated under vacuo, and a solid residue obtained was obtained, which was washed with *n*-pentane (5 mL). White solid compound obtained in each case. The conversion of amines was calculated from isolated pure products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02302.

Tabulated bond lengths and bond angles of **1a**−**c**, **2a**, **2c**, and **3a**; illustrated solid-state structures; NMR spectral data of various urea derivatives. (PDF)

X-ray crystallographic information for **1a**. (CIF)

X-ray crystallographic information for **1b**. (CIF)

X-ray crystallographic information for **1c**. (CIF)

X-ray crystallographic information for **2a**. (CIF)

X-ray crystallographic information for **2c**. (CIF)

X-ray crystallographic information for **3a**. (CIF)

X-ray crystallographic information for **4c**. (CIF)

X-ray crystallographic information for **6c**. (CIF)

X-ray crystallographic information for **7b**. (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tpanda@iith.ac.in. Fax: +91(40) 2301 6032.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568−2570. (b) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *Org. Lett.* **2001**, *3*, 3091−3094. (c) Hong, S.; Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 15878−15892. (d) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *J. Org. Chem.* **2004**, *69*, 1038−1052. (e) Seyam, A. M.; Stubbert, B. D.; Jensen, T. R.; O'Donnell, J. J., III; Stern, C. L.; Marks, T. J. *Inorg. Chim. Acta* **2004**, *357*, 4029−4035. (f) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686. (g) Ryken, S. A.; Schafer, L. L. *Acc. Chem. Res.* **2015**, *48*, 2576−2586.

(2) Reviews: (a) Nobis, M. B.; Drießen-Hölscher, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 3983−3985. (b) Brunet, J.-J.; Neibecker, D. *Catalytic Heterofunctionalization,* Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; pp 91−141. (c) Seayad, J.; Tillack, A.; Hartung, C. G.; Beller, M. *Adv. Synth. Catal.* **2002**, *344*, 795−813. (d) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104−114. (e) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, *2003*, 935−946. (f) Roesky, P. W.; Müller, T. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2708−2710. (g) Hartwig, J. F. *Pure Appl. Chem.* **2004**, *76*, 507−516. (h) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367−391. (i) Widenhoefer, R. A.; Han, X. *Eur. J. Org. Chem.* **2006**, *2006*, 4555−4563.

(3) (a) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 354−358. (b) Kaspar, L. T.; Fingerhut, B.; Ackermann, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5972−5974. (c) Heutling, A.; Pohlki, F.; Bytschkov, I.; Doye, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2951−2954. (d) Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 5608−5609. (e) Takemiya, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 6042−6043. (f) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857−10858. (g) Utsunomiya, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 14286−14287. (h) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828−1839. (i) Brunet, J.-J.; Chu, N. C.; Diallo, O. *Organometallics* **2005**, *24*, 3104−3110. (j) Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070−1071. (k) Brouwer, C.; He, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1744−1747. (l) Han, X.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1747−1749. (m) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066−9073. (n) Kang, J.-E.; Kim, H.-B.; Lee, J.-W.; Shin, S. *Org. Lett.* **2006**, *8*, 3537−3540. (o) Zulys, A.; Dochnahl, M.; Hollmann, D.; Löhnwitz, K.; Herrmann, J.-S.; Roesky, P. W.; Blechert, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7794−7798. (p) Dochnahl, M.; Pissarek, J.-W.; Blechert, S.; Löhnwitz, K.; Roesky, P. W. *Chem. Commun.* **2006**, 3405−3407. (q) Meyer, N.; Löhnwitz, K.; Zulys, A.; Roesky, P. W.; Dochnahl, M.; Blechert, S. *Organometallics* **2006**, *37*, 3779−3783. (r) Dochnahl, M.; Löhnwitz, K.; Pissarek, J.-W.; Biyikal, M.; Schulz, S.; Schön, S.; Meyer, N.; Roesky, P. W.; Blechert, S. *Chem. - Eur. J.* **2007**, *13*, 6654−6666.

(4) (a) Kim, Y. K.; Livinghouse, T.; Bercaw, J. E. *Tetrahedron Lett.* **2001**, *42*, 2933−2935. (b) Kim, Y. K.; Livinghouse, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 3645−3647. (c) Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560−9561. (d) O'Shaughnessy, P. N.; Knight, P. D.; Morton, C.; Gillespie, K. M.; Scott, P. *Chem. Commun.* **2003**, 1770−1771. (e) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *Chem. - Eur. J.* **2003**, *9*, 4796−4810. (f) Gribkov, D. V.; Hultzsch, K. C. *Chem. Commun.* **2004**, 730−731. (g) Hultzsch, K. C.; Hampel, F.; Wagner, T. *Organometallics* **2004**, *23*, 2601−2612. (h) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748−3759. (i) Riegert, D.; Collin, J.; Meddour, A.; Schulz, E.; Trifonov, A. *J. Org. Chem.* **2006**, *71*, 2514−2517. (j) Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Chem. - Eur. J.* **2001**, *7*, 3078−3085. (k) Meyer, N.; Zulys, A.; Roesky, P. W. *Organometallics* **2006**, *25*, 4179−4182. (l) Rastätter, M.; Zulys, A.; Roesky, P. W. *Chem. - Eur. J.* **2007**, *13*, 3606−3616. (m) Haskel, A.; Straub, T.; Eisen, M. E. *Organometallics* **1996**, *15*, 3773−3775. (n) Wang, J.; Dash, A. K.; Kapon, M.; Berthet, J.-C.; Ephritikhine, M.; Eisen, M. S. *Chem. - Eur. J.* **2002**, *8*, 5384−5396. (o) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.;

DOI: 10.1021/acs.inorgchem.5b02302
Inorg. Chem. 2016, 55, 1142−1153

Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017−5035. (p) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149−6167.

(5) (a) Ates, A.; Quinet, C. *Eur. J. Org. Chem.* **2003**, *2003*, 1623−1626. (b) Martínez, P. H.; Hultzsch, K. C.; Hampel, F. *Chem. Commun.* **2006**, 2221−2223. (c) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042−2043. (d) Datta, S.; Roesky, P. W.; Blechert, S. *Organometallics* **2007**, *26*, 4392−4394. (e) Datta, S.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2008**, *27*, 1207−1213.

(6) (a) Pi, C.; Zhang, Z.; Pang, Z.; Zhang, J.; Luo, J.; Chen, Z.; Weng, L.; Zhou, X. *Organometallics* **2007**, *26*, 1934. (b) Zhang, J.; Cai, R.; Weng, L.; Zhou, X. *Organometallics* **2004**, *23*, 3303. (c) Zhang, J.; Cai, R.; Weng, L.; Zhou, X. *Organometallics* **2003**, *22*, 5385. (d) Zhang, J.; Cai, R.; Weng, L.; Zhou, X. *J. Organomet. Chem.* **2003**, *672*, 94. (e) Ma, L.; Zhang, J.; Cai, R.; Chen, Z.; Weng, L.; Zhou, X. *J. Organomet. Chem.* **2005**, *690*, 4926. (f) Trifonov, A. A.; Lyubov, D. M.; Fedorova, E. A.; Skvortsov, G. G.; Fukin, G. K.; Kurskii, Y. A.; Bochkarev, M. N. *Russ. Chem. Bull.* **2006**, *55*, 435. (g) Tu, J.; Li, W.; Xue, M.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2013**, *42*, 5890. (h) Du, Z.; Zhou, H.; Yao, H.; Zhang, Y.; Yao, Y.; Shen, Q. *Chem. Commun.* **2011**, *47*, 3595−3597.

(7) (a) Zhang, W. X.; Nishiura, M.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 16788. (b) Zhang, W. X.; Hou, Z. *Org. Biomol. Chem.* **2008**, *6*, 1720. (c) Zhang, W. X.; Nishiura, M.; Hou, Z. *Chem. - Eur. J.* **2007**, *13*, 4037. (d) Zhang, W. X.; Nishiura, M.; Hou, Z. *Synlett* **2006**, *2006*, 1213. (e) Zhang, W. X.; Li, D.; Wang, Z.; Xi, Z. *Organometallics* **2009**, *28*, 882. (f) Shen, H.; Chan, H.; Xie, Z. *Organometallics* **2006**, *25*, 5515. (g) Du, Z.; Li, W.; Zhu, X.; Xu, F.; Shen, Q. *J. Org. Chem.* **2008**, *73*, 8966. (h) Zhu, X. H.; Du, Z.; Xu, F.; Shen, Q. *J. Org. Chem.* **2009**, *74*, 6347. (i) Kim, Y. K.; Livinghouse, T.; Bercaw, J. E. *Tetrahedron Lett.* **2001**, *42*, 2933. (j) Kim, Y. K.; Livinghouse, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 3645. (k) Zhou, S. L.; Wang, S.; Yang, G.; Li, Q.; Zhang, L.; Yao, Z.; Zhou, Z.; Song, H. *Organometallics* **2007**, *26*, 3755. (l) Li, Q. H.; Wang, S.; Zhou, S.; Yang, G.; Zhu, X.; Liu, Y. *J. Org. Chem.* **2007**, *72*, 6763. (m) Liu, C.; Zhou, S.; Wang, S.; Zhang, L.; Yang, G. *Dalton Trans.* **2010**, *39*, 8994.

(8) (a) Behrle, A. C.; Schmidt, J. A. R. *Organometallics* **2013**, *32*, 1141. (b) Tu, J.; Li, W.; Xue, M.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2013**, *42*, 5890. (c) Li, Z.; Xue, M.; Yao, H.; Sun, H.; Zhang, Y.; Shen, Q. *J. Organomet. Chem.* **2012**, *713*, 27. (d) Cao, Y.; Du, Z.; Li, W.; Li, J.; Zhang, Y.; Xu, F.; Shen, Q. *Inorg. Chem.* **2011**, *50*, 3729. (e) Zhang, X.; Wang, C.; Qian, C.; Han, F.; Xu, F.; Shen, Q. *Tetrahedron* **2011**, *67*, 8790. (f) Du, Z.; Zhou, H.; Yao, H.; Zhang, Y.; Yao, Y.; Shen, Q. *Chem. Commun.* **2011**, *47*, 3595. (g) Yi, W.; Zhang, J.; Hong, L.; Chen, Z.; Zhou, X. *Organometallics* **2011**, *30*, 5809.

(9) (a) Durant, G. J. *Chem. Soc. Rev.* **1985**, *14*, 375. (b) Berlinck, R. G. S. *Nat. Prod. Rep.* **1996**, *13*, 377. (c) Berlinck, R. G. S. *Nat. Prod. Rep.* **1999**, *16*, 339. (d) Heys, L.; Moore, C. G.; Murphy, P. J. *Chem. Soc. Rev.* **2000**, *29*, 57. (e) Berlinck, R. G. S. *Nat. Prod. Rep.* **2002**, *19*, 617.

(10) (a) Berlinck, R. G. S.; Burtoloso, A. C. B.; Kossuga, M. H. *Nat. Prod. Rep.* **2008**, *25*, 919−954. (b) Castagnolo, D.; Schenone, S.; Botta, M. *Chem. Rev.* **2011**, *111*, 5247−5300. (c) Berlinck, R. G. S.; Trindade-Silva, A. E.; Santos, M. F. C. *Nat. Prod. Rep.* **2012**, *29*, 1382−1406. (d) Schmuck, C. *Coord. Chem. Rev.* **2006**, *250*, 3053−3067. (e) Berlinck, R. G. S.; Burtoloso, A. C. B.; Trindade-Silva, A. E.; Romminger, S.; Morais, R. P.; Bandeira, K.; Mizuno, C. M. *Nat. Prod. Rep.* **2010**, *27*, 1871−1907. (f) Berlinck, R. G. S. *Nat. Prod. Rep.* **1996**, *13*, 377−409.

(11) (a) Ishikawa, T.; Kumamoto, T. *Synthesis* **2006**, *2006*, 737−752. (b) Ishikawa, T. *Chem. Pharm. Bull.* **2010**, *58*, 1555−1564. (c) Taylor, J. E.; Bull, S. D.; Williams, J. M. J. *Chem. Soc. Rev.* **2012**, *41*, 2109−2121. (d) Coles, M. P. *Chem. Commun.* **2009**, 3659−3676.

(12) (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91. (c) Coles, M. P. *Dalton Trans.* **2006**, 985. (d) Edelmann, F. T. *Chem. Soc. Rev.* **2009**, *38*, 2253. (e) Edelmann, F. T. *Adv. Organomet. Chem.* **2008**, *57*, 183. (f) Rowley, C. N.; DiLabio, G. A.; Barry, S. T. *Inorg. Chem.* **2005**, *44*, 1983. (g) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924. (h) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274. (i) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. *Organometallics* **1998**, *17*, 4042. (j) Milanov, A. P.; Thiede, T. B.; Devi, A.; Fischer, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 17062. (k) Ong, T. G.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 8100. (l) Rohde, J. U.; Lee, W. T. *J. Am. Chem. Soc.* **2009**, *131*, 9162. (m) Shen, H.; Chan, H. S.; Xie, Z. *J. Am. Chem. Soc.* **2007**, *129*, 12934.

(13) (a) Gallou, I. *Org. Prep. Proced. Int.* **2007**, *39*, 355. (b) McMorris, T. C.; Chimmani, R.; Alisala, K.; Staake, M. D.; Banda, G.; Kelner, M. J. *J. Med. Chem.* **2010**, *53*, 1109. (c) Maier, T.; Beckers, T.; Baer, T.; Vennemann, M.; Gekler, V.; Zimmermann, A.; Gimmnich, P.; Padiya, K.; Joshi, H.; Joshi, U.; Makhija, M.; Harel, D. U.S. Patent 20110021494. (d) Feng, Y.; Lograsso, P.; Schroeter, T.; Yin, Y. U. S. Patent 200899642. (e) Kim, J.; Davis, R.; Zentel, R. *J. Colloid Interface Sci.* **2011**, *359*, 428.

(14) (a) Diaz, D. J.; Darko, A. K.; McElwee-White, L. *Eur. J. Org. Chem.* **2007**, *2007*, 4453. (b) Artuso, E.; Degani, I.; Fochi, R.; Magistris, C. *Synthesis* **2007**, *2007*, 3497−3506. (c) Padiya, K. J.; Gavade, S.; Kardile, B.; Tiwari, M.; Bajare, S.; Mane, M.; Gaware, V.; Varghese, S.; Harel, D.; Kurhade, S. *Org. Lett.* **2012**, *14*, 2814−2817. (d) Mizuno, T.; Nakai, T.; Mihara, M. *Synthesis* **2009**, *2009*, 2492−2496. (e) Thalluri, K.; Manne, S. R.; Dev, D.; Mandal, B. *J. Org. Chem.* **2014**, *79*, 3765−3775. (f) Spyropoulos, C.; Kokotos, C. G. *J. Org. Chem.* **2014**, *79*, 4477−4483. (g) Spyropoulos, C.; Kokotos, C. G. *J. Org. Chem.* **2014**, *79*, 4477−4483. (h) Vinogradova, E. V.; Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2012**, *134*, 11132−11135. (I) Vasantha, B.; Hemantha, H. P.; Sureshbabu, V. V. *Synthesis* **2010**, *2010*, 2990−2996.

(15) (a) Dubé, P.; Nathel, N. F. F.; Vetelino, M.; Couturier, M.; Aboussafy, C. L.; Pichette, S.; Jorgensen, M. L.; Hardink, M. *Org. Lett.* **2009**, *11*, 5622−5625. (b) Le, H. V.; Ganem, B. *Org. Lett.* **2011**, *13*, 2584−2585. (c) Han, C.; Porco, J. A. *Org. Lett.* **2007**, *9*, 1517−1520. (d) Lee, H.-G.; Kim, M.-J.; Park, S.-E.; Kim, J.-J.; Lee, S.-G.; Yoon, Y.-J.; Kim, B. *Synlett* **2009**, *2009*, 2809−2814. (e) Hemantha, H. P.; Chennakrishnareddy, G.; Vishwanatha, T. M.; Sureshbabu, V. V. *Synlett* **2009**, *2009*, 407−410. (f) Lebel, H.; Leogane, O. *Org. Lett.* **2006**, *8*, 5717−5720. (g) Bertrand, M. B.; Wolfe, J. P. *Tetrahedron* **2005**, *61*, 6447−6459. (h) Bertrand, M. B.; Wolfe, J. P. *Tetrahedron* **2005**, *61*, 6447−6459. (i) McLaughlin, M.; Palucki, M.; Davies, I. W. *Org. Lett.* **2006**, *8*, 3311−3314. (j) Fritz, J. A.; Nakhla, J. P.; Wolfe, J. P. *Org. Lett.* **2006**, *8*, 2531−2534. (k) Marinescu, L.; Thinggaard, J.; Thomsen, I. B.; Bols, M. *J. Org. Chem.* **2003**, *68*, 9453−9455. (l) Paz, J.; Pérez-Balado, C.; Iglesias, B.; Muñoz, L. *J. Org. Chem.* **2010**, *75*, 8039−8047. (m) Lee, S.-H.; Matsushita, H.; Clapham, B.; Janda, K. D. *Tetrahedron* **2004**, *60*, 3439−3443.

(16) Karmel, I. S. R.; Tamm, M.; Eisen, M. S. *Angew. Chem., Int. Ed.* **2015**, *54*, 12422.

(17) Tamm, M.; Petrovic, D.; Randoll, S.; Beer, S.; Bannenberg, T.; Jones, P. G.; Grunenberg, J. *Org. Biomol. Chem.* **2007**, *5*, 523−530.

(18) (a) Tamm, M.; Randoll, S.; Bannenberg, T.; Herdtweck, E. *Chem. Commun.* **2004**, 876−877. (b) Tamm, M.; Beer, S.; Herdtweck, E. *Z. Naturforsch.* **2004**, *59b*, 1497−1504. (c) Tamm, M.; Randoll, S.; Herdtweck, E.; Kleigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton Trans.* **2006**, 459−467. (d) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890−8894. (e) Beer, S.; Brandhorst, K.; Grunenberg, J.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Org. Lett.* **2008**, *10*, 981−984. (f) Stelzig, S. H.; Tamm, M.; Waymouth, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6064−6070. (g) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534−1545.

(19) Kuhn, N.; Göhner, M.; Grathwohl, M.; Wiethoff, J.; Frenking, G.; Chen, Y. *Z. Anorg. Allg. Chem.* **2003**, *629*, 793−802.

(20) (a) Trambitas, A. G.; Panda, T. K.; Tamm, M. *Z. Anorg. Allg. Chem.* **2010**, *636*, 2156−2171. (b) Wu, X.; Tamm, M. *Coord. Chem. Rev.* **2014**, *260*, 116−138. (c) Panda, T. K.; Randoll, S.; Hrib, C. G.; Jones, P. G.; Bannenberg, T.; Tamm, M. *Chem. Commun.* **2007**, 5007−5009. (d) Beer, S.; Brandhorst, K.; Grunenberg, J.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Org. Lett.* **2008**, *10*, 981−984. (e) Petrovic, D.; Hill,

DOI: 10.1021/acs.inorgchem.5b02302
Inorg. Chem. 2016, 55, 1142−1153

L. M. R.; Jones, P. G.; Tolman, W. B.; Tamm, M. *Dalton Trans.* **2008**, 887−894. (f) Petrovic, D.; Hrib, C. G.; Randoll, S.; Jones, P. G.; Tamm, M. *Organometallics* **2008**, *27*, 778−783. (g) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534−1545. (h) Panda, T. K.; Trambitas, A. G.; Bannenberg, T.; Hrib, C. G.; Randoll, S.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2009**, *48*, 5462−5472. (i) Trambitas, A.; Panda, T. K.; Jenter, J.; Roesky, P.; Daniliuc, C.-G.; Hrib, C.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2010**, *49*, 2435−2446. (j) Panda, T. K.; Hrib, C. G.; Jones, P. G.; Tamm, M. *J. Organomet. Chem.* **2010**, *695*, 2768−2773. (k) Tamm, M.; Trambitas, A. G.; Hrib, C.; Jones, P. G. *Terrae Rarae* **2010**, *7*, 1−4. (l) Trambitas, A. G.; Melcher, D.; Hartenstein, L.; Roesky, P. W.; Daniliuc, C.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2012**, *51*, 6753−6761. (m) Karmel, I.; Botoshansky, M.; Tamm, M.; Eisen, M. S. *Inorg. Chem.* **2014**, *53*, 694−696.

(21) Panda, T. K.; Hrib, C. G.; Jones, P. G.; Jenter, J.; Roesky, P. W.; Tamm, M. *Eur. J. Inorg. Chem.* **2008**, *2008*, 4270.

(22) Glöckner, A.; Bannenberg, T.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Inorg. Chem.* **2012**, *51*, 4368−4378.

(23) (a) Glöge, T.; Petrovic, D.; Hrib, C.; Jones, P. G.; Tamm, M. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4538−4546. (b) Trambitas, A. G.; Yang, J.; Melcher, D.; Daniliuc, C. G.; Jones, P. G.; Xie, Z.; Tamm, M. *Organometallics* **2011**, *30*, 1122−1129. (c) Sharma, M.; Yameen, H.; Tumanskii, B.; Filimon, S.-A.; Tamm, M.; Eisen, M. *J. Am. Chem. Soc.* **2012**, *134*, 17234−17244. (d) Wu, X.; Tamm, M. *Beilstein J. Org. Chem.* **2011**, *7*, 82−93. (e) Tamm, M.; Wu, X. *Chemistry Today* **2010**, *28*, 60−63. (f) Volbeda, J.; Jones, P. G.; Tamm, M. *Inorg. Chim. Acta* **2014**, *422*, 158−166. (g) Nomura, K.; Bahuleyan, B.; Zhang, S.; Veeresha Sharma, P.; Katao, S.; Igarashi, A.; Inagaki, A.; Tamm, M. *Inorg. Chem.* **2014**, *53*, 607−623. (h) Shoken, D.; Sharma, M.; Botoshansky, M.; Tamm, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2013**, *135*, 12592−12595. (i) Lysenko, S.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *J. Organomet. Chem.* **2013**, *744*, 7−14. (j) Apisuk, W.; Trambitas, A. G.; Kitiyanan, B.; Tamm, M.; Nomura, K. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 2575−2580. (k) Haberlag, B.; Freytag, M.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 13019−13022. (l) Nomura, K.; Fukuda, H.; Apisuk, W.; Trambitas, A.; Kitiyanan, B.; Tamm, M. *J. Mol. Catal. A: Chem.* **2012**, *363*−*364*, 501−511. (m) Tamm, M.; Randoll, S.; Herdtweck, E.; Kleigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton Trans.* **2006**, 459−467. (n) Stelzig, S. H.; Tamm, M.; Waymouth, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6064−6070. (o) Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890−8894. (p) Beer, S.; Brandhorst, K.; Grunenberg, J.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Org. Lett.* **2008**, *10*, 981−984. (q) Beer, S.; Brandhorst, K.; Hrib, C. G.; Wu, X.; Haberlag, B.; Grunenberg, J.; Jones, P. G.; Tamm, M. *Organometallics* **2009**, *28*, 1534−1545. (r) Haberlag, B.; Wu, X.; Brandhorst, K.; Grunenberg, J.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Chem. - Eur. J.* **2010**, *16*, 8868−8877. (s) Tamm, M.; Wu, X. *Chim. Oggi.* **2010**, *28*, 10−13. (t) Wu, X.; Tamm, M. *Beilstein J. Org. Chem.* **2011**, *7*, 82−93.

(24) Panda, T. K.; Tsurugi, H.; Pal, K.; Kaneko, H.; Mashima, K. *Organometallics* **2010**, *29*, 34−37.

(25) Tamm, M.; Randoll, S.; Herdtweck, E.; Kleigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. *Dalton Trans.* **2006**, 459−467.

(26) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2007**, *26*, 2694.

(27) Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2003**, *22*, 4522.

(28) (a) Tang, J.; Mohan, T.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 4931. (b) Weiss, K.; Hoffmann, K. Z. *Z. Naturforsch., B: J. Chem. Sci.* **1987**, *42*, 769. (c) Kogon, I. C. *J. Am. Chem. Soc.* **1956**, *78*, 4911.

(29) (a) Wu, Y.; Wang, S.; Zhu, X.; Yang, G.; Wei, Y.; Zhang, L.; Song, H- B. *Inorg. Chem.* **2008**, *47*, 5503. (b) Zhu, X.; Fan, J.; Wu, Y.; Wang, S.; Zhang, L.; Yang, G.; Wei, Y.; Yin, C.; Zhu, H.; Wu, S.; Zhang, H. *Organometallics* **2009**, *28*, 3882. (c) Zhang, J.; Han, F.; Han, Y.; Chen, Z.; Zhou, X. *Dalton Trans.* **2009**, 1806.

(30) Wang, H.; Chan, H.-S.; Okuda, J.; Xie, Z. *Organometallics* **2005**, *24*, 3118.

(31) Matsui, S.; Yoshida, Y.; Takagi, Y.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2004**, *689*, 1155.

(32) Altomare, A.; Burla, M. C.; Camalli, G.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(33) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.

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