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Catalytic Imido-Transfer Reactions of Well-Defined Silica-Supported Titanium Imido Complexes Prepared via Surface Organometallic Chemistry

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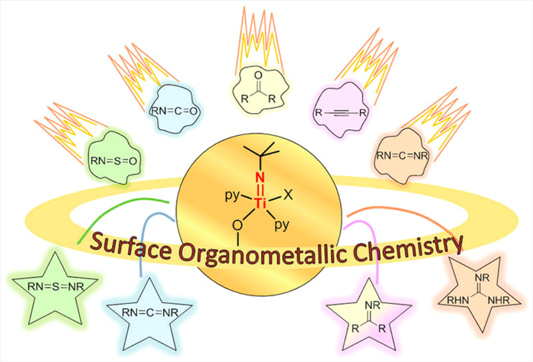
ABSTRACT: We expand the series of well-defined silica-supported titanium imido complexes of general formula $(\equiv SiO)Ti(=N\mathit{t}Bu)X(py)_n$ prepared via surface organometallic chemistry in order to analyze the effect of the X igand on their catalytic properties. Two new surface complexes, $(\equiv SiO)Ti(=N\mathit{t}Bu)Cl(py)_2$ (**2s**) and $(\equiv SiO)Ti(=N\mathit{t}Bu)Cp(py)$ (**3s**), have been prepared and characterized with physicochemical techniques, and their performance in oxo/imido heterometathesis and other catalytic imido-transfer reactions has been studied and compared to that of the previously reported catalyst $(\equiv SiO)Ti(=N\mathit{t}Bu)(Me_2Pyr)(py)_2$ (**1s**; Me_2Pyr = 2,5-dimethylpyrrolyl).

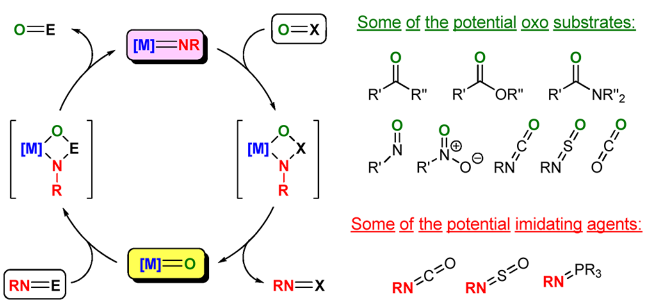


■ INTRODUCTION

Surface organometallic chemistry (*SOMC*)[1] is a growing interdisciplinary field that utilizes coordination and organometallic molecular precursors for the preparation of well-defined metal sites covalently attached (*grafted*) to the surface of a solid support in order to gain insight into the structures of the active species and reaction mechanisms on the surfaces of classical heterogeneous catalysts, as well as to discover and develop new catalytic reactions. The SOMC approach is based on a rigorous control of the interaction of well-defined molecular complexes with a carefully prepared support having a desired density of surface functionalities regarded as ligands entering the coordination sphere of the metal, followed by detailed characterization of the resulting surface species with physicochemical techniques, study of the ligand effects, and building of the structure−activity relationships similarly to what is typically done in molecular chemistry and catalysis. Briefly speaking, SOMC considers the surface as an additional dimension for the application of the basic principles of coordination and organometallic chemistry.

One of the important features of SOMC is the possibility to design and stabilize the supported species that would readily decompose in solution via bimolecular pathways. Remarkable examples include silica-supported early-transition-metal hydrides[2a] and low-coordinate isolated single sites.[2b] Our group has been developing catalytic oxo/imido heterometathesis reactions[3] where the interconversion of the transition-metal oxo and imido components via [2 + 2] cycloaddition/cycloreversion steps constitutes a catalytic cycle, resulting in the imidation of various oxo substrates (Scheme 1). On the basis of the stoichiometric reactivity of transition-metal imido complexes[4] it was clear that the most active catalysts should be found in the left part of the d block of the Periodic Table, in particular among group 4 metals; however, the instability of the terminal oxo derivatives of these metals (the formation of oxo-bridged oligomers, which in this case means deactivation) prevented the development of this chemistry.

Scheme 1. Oxo/Imido Heterometathesis Catalytic Cycle



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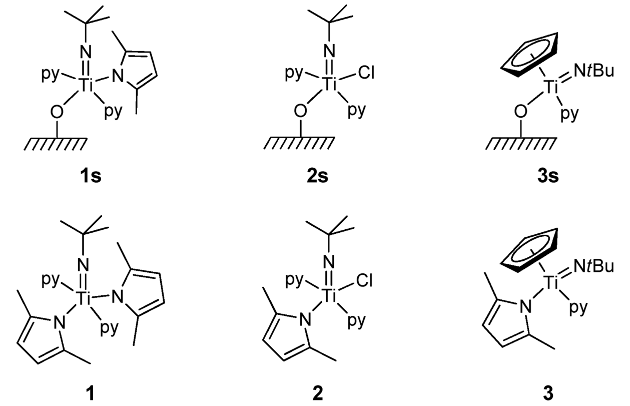
SOMC provided an elegant solution to this problem: if a properly designed monomeric imido complex is grafted onto the surface, the metal site will remain monomeric and the oligomerization of the transient oxo intermediate will be avoided.[5] We have recently reported the preparation of the well-defined silica-supported Ti imido complex[6] [(≡SiO)Ti(═N*t*Bu)(Me$_2$Pyr)(py)$_2$] (**1s**) (Chart 1; Me$_2$Pyr = 2,5-dimethylpyrrolyl) that displayed unprecedented activity in the heterometathetical imidation of carbonyl compounds with *N*-sulfinylamines.[6,7] In this report we continue to explore the chemistry of silica-supported Ti imides and begin a more detailed study of the electronic effects of the ligands on the catalytic activity. We describe here two new well-defined silica-supported Ti imido complexes where the ancillary X ligand (Me$_2$Pyr) is replaced with a very poorly electron donating chloride or a strongly donating Cp ligand, [(≡SiO)Ti(═N*t*Bu)Cl(py)$_2$] (**2s**) and [(≡SiO)Ti(═N*t*Bu)Cp(py)] (**3s**), prepared from the corresponding molecular 2,5-dimethylpyrrolyl derivatives **2** and **3** (Chart 1), as well as a study of the performance of the surface complexes **1s**−**3s** in oxo/imido heterometathesis and other catalytic imido-transfer reactions.

Chart 1. Grafted and Molecular Complexes Studied in This Work

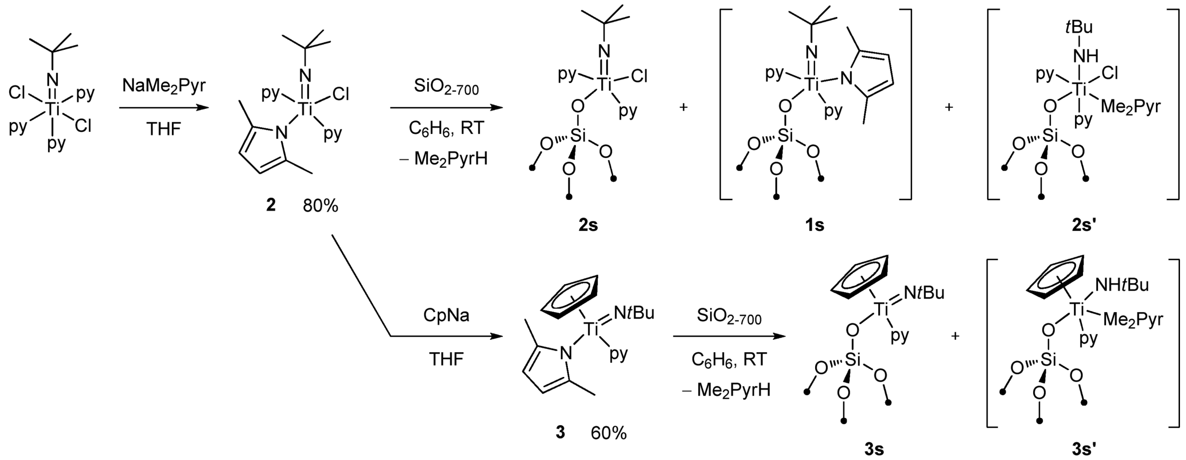


RESULTS AND DISCUSSION

Synthesis of the Molecular Precursors. The proper choice of a suitable molecular precursor for grafting is a crucial point in SOMC. In our work we have defined the following criteria for the design of the molecular precursors. (i) The complexes should be monomeric and contain a terminal imido ligand as required for catalysis; however, excessive steric bulk that can suppress the reactivity is not desirable. This criterion can be problematic for early-transition-metal imides that often tend to lose the supporting L ligands (especially when X ligands are sufficiently electron donating), leading to the dimerization of the resulting coordinatively unsaturated species[8] (3-coordinated in the case of group 4). (ii) The imido moiety bound to early transition metals is highly reactive and can be easily protonated by the surface silanol groups during grafting, leading to the supported amido species. Hence, the molecular precursor should also bear a more reactive, easily cleavable X ligand that will play the role of an anchoring site. An alkyl group would be the ideal choice; however, for the reasons mentioned above, so far we have not been able to prepare monomeric Ti imido alkyls analogous to the respective group 5 systems.[5,9] Previous studies have shown that the 2,5-dimethylpyrrolyl ligand[10] is an excellent leaving group for grafting early-transition-metal alkylidene[11] and imido[6] complexes on silica. It is sufficiently reactive to be easily and selectively cleaved with the surface silanols, while the releasing pyrrole (Me$_2$PyrH) serves as a convenient probe for quantification of the grafting reaction by analysis of the liquid phase. In addition, its variable hapticity and moderate steric bulk may be advantageous to favor the monomeric structures of the complexes. (iii) A *tert*-butyl substituent at the imido group is chosen because its quaternary carbon is very sensitive to the state of the imido ligand and provides a convenient tool for its characterization by solid-state NMR. Protonation typically leads to a 5−10 ppm upfield shift in ^{13}C and the corresponding resonances for Ti imido, amido, and amino species can be expected at roughly 70, 60, and 50 ppm, respectively.[12] In addition, the starting material [Ti(═N*t*Bu)Cl$_2$(py)$_3$] is readily available via Mountford's protocol.[13] (iv) To enable unambiguous assignments in solid-state NMR, it is also desirable that the ligands be simple and symmetrical and give distinctive NMR signatures. These requirements lead to the following general structure [Ti(═N*t*Bu)(Me$_2$Pyr)(X)(L)$_n$]. We report here the synthesis of the monopyrrolyl monochloride complex **2** (X = Cl, L = py, *n* = 2) and show that it can be further used as a precursor for introducing other X ligands via substitution of the chloride.

Treatment of [Ti(═N*t*Bu)Cl$_2$(py)$_3$] with 1 equiv of NaMe$_2$Pyr or LiMe$_2$Pyr in THF leads to a selective substitution

Scheme 2. Preparation of Molecular and Grafted Complexes



of one chloride ligand and isolation of **2** in high yield as a yellow powder that can be recrystallized from Et_2O/pentane to give XRD-suitable orange crystals. Complex **2** reacts with 1 equiv of CpNa to give **3**, which crystallizes from toluene as red crystals (Scheme 2). Single-crystal X-ray diffraction studies show that both complexes are monomeric, the geometries being shown in Figure 1. The structure of **2** is very similar to that of the previously characterized bis-pyrrolyl complex **1**[6] and can be described as a trigonal bipyramid with two pyridines in the apical positions. The molecule of the Cp derivative **3** has a typical piano-stool geometry. The Ti═N bond lengths in complexes **1**−**3** increase in the order **2** < **1** < **3** and are 1.686(2), 1.695(2), and 1.705(1) Å, respectively, which correlates with the donating ability of the ancillary ligands (see below). Me_2Pyr ligands in all three complexes are flat and coordinated in an η^1 fashion. Similarly to **1**, $Ti-N_{Me_2Pyr}$ bond lengths in **2** and **3** are relatively long (ca. 2.03−2.09 Å), consistent with the weak π-donating character of the pyrrolyl ligand.[14] However, the angles $\angle Ti-N_{Me_2Pyr}-Me_2Pyr_{centroid}$ are only slightly distorted from 180° (ca. 158° for **1**, 162° for **2**, and 178° for **3**) and thus some extent of π-donation is not excluded.[10a,15] The pyrrolyl ring in **2** lies in the equatorial plane. Two sets of resonances for the methyl and CH groups of the Me_2Pyr ligand are observed in the ^1H and ^{13}C NMR of **2** (analogously to **1**), and only one is observed for the Cp derivative **3**, indicating a lower rotation barrier around the Ti−N bond in the latter case.

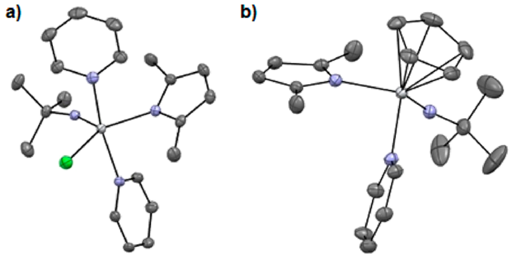


Figure 1. Thermal ellipsoid plots of (a) [Ti(═N*t*Bu)Cl(Me_2Pyr)($py)_2$] (**2**) (only one of the two independent molecules is shown) and (b) [Ti(═N*t*Bu)Cp(Me_2Pyr)(py)] (**3**) at the 50% probability level. Hydrogen atoms are omitted.

Grafting. Complexes **2** and **3** were grafted onto the surface of silica partially dehydroxylated at 700 °C (SiO_{2-700}) in a standard manner—by slow stirring of a solution of the complex in benzene with a suspension of silica overnight, subsequent decanting of the solution, and drying the solid material under high vacuum. In both cases 0.8−0.9 equiv of Me_2PyrH per Ti is released during grafting according to NMR quantification of the combined washings/volatiles, suggesting the predominant formation of surface complexes **2s** and **3s** (Scheme 2; the scheme also shows the possible expected byproducts, see below). Elemental analysis of the grafted materials reveals 1.1 wt % of Ti in both cases (corresponding to 0.23 mmol of Ti g^{-1}) and gives a Ti/N/C/Cl ratio of 1/3.4/14.2/1.0 for **2s** and a Ti/N/C ratio of 1/2.7/14.8 for **3s**, close to the expected values of 1/3/14/1 and 1/2/14, respectively. IR spectroscopy confirms almost quantitative consumption of the surface silanol groups (the band at 3747 cm^{-1}) and the appearance of ν_{CH} and δ_{CH} vibrations of the ligands (Figure 2).

Solid-state NMR is particularly helpful in elucidating the structures of surface complexes (Figure 3). ^{13}C CP MAS spectra of both materials show distinct resonances of the ortho, para, and meta CH carbons of pyridine at ca. 151, 138, and 123 ppm, respectively, and a signal of the CH_3 groups of the N*t*Bu ligand at ca. 30 ppm. The Cp ring of **3s** appears at 109 ppm. Most importantly, the characteristic quaternary carbon of the N*t*Bu group is clearly observed in both spectra (at ca. 71 and 68 ppm for **2s** and **3s**, respectively). All resonances correlate well with those in the liquid-state spectra of the molecular precursors (see the Supporting Information). The high resolution of the spectra allows for tentative identification of the minor byproduct surface species. The peaks at 115 and 16 ppm in the spectrum of **3s** can be assigned to the *Cp* and *Me*$_2$Pyr ligands of the protonated species **3s′** (Scheme 2), the quaternary carbon of NH*t*Bu being visible as a tiny peak at 59 ppm (see the Supporting Information for the enlarged picture). The signals at 106 and 16 ppm in the spectrum of **2s** correlate well with those of the surface complex **1s** that has been characterized before[6] and could arise from the substitution of the chloride instead of the Me_2Pyr ligand in **2** during grafting. On the other hand, these signals could be also attributed to the protonated complex **2s′** (Scheme 2). The peak at 48 ppm in this case may correspond to NH*t*Bu of **2s′**; however, such a resonance should be expected at slightly lower field (as in **3s′**) and we would rather ascribe the signal at 48 ppm to a trace amount of *t*$BuNH_2$ (the same chemical shift in liquid-state NMR) that is sometimes observed in the spectra of different grafted N*t*Bu complexes, likely due to adventitious moisture during the measurement, even though neither option can be excluded. The trace signals corresponding to the remaining Me_2Pyr ligand are also detectable in the ^1H MAS NMR of **2s** and **3s** (see the Supporting Information). On the basis of the intensities of the peaks together with the elemental analysis data and the amount of Me_2PyrH released during grafting, the abundance of these minor surface forms can be estimated as no more than 10%.

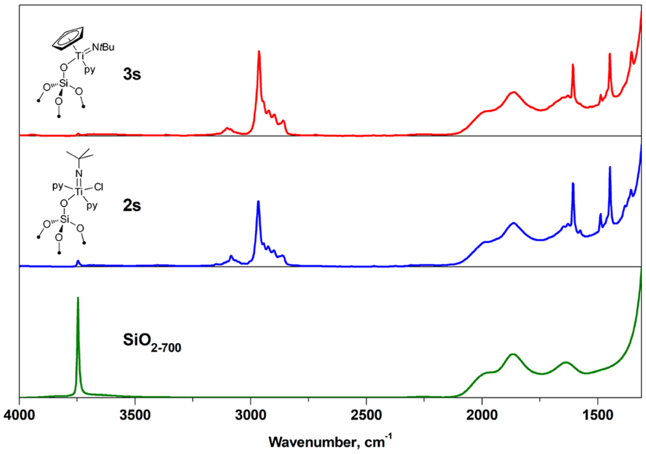


Figure 2. IR spectra of SiO_{2-700} and grafted materials.

Catalytic Studies. The materials **1s**−**3s** were investigated in a set of catalytic test reactions that are typically associated with imido complexes. Since the main focus of our research is catalytic oxo/imido heterometathesis, we have first tested the new catalysts in the imidation of carbonyl compounds with *N*-sulfinylamines. The reaction of benzophenone with *N*-sulfinyl-*p*-toluidine (TolNSO) in boiling heptane (98 °C) at 1 mol % catalyst loading was used as a standard test, and TOF after the first 15 min of the reaction and half-conversion time were used to evaluate the catalyst performance, as has been established before.[6] The results are shown in Table 1 and Figure 4a. From these data we can see that (i) the nature of the ancillary ligands

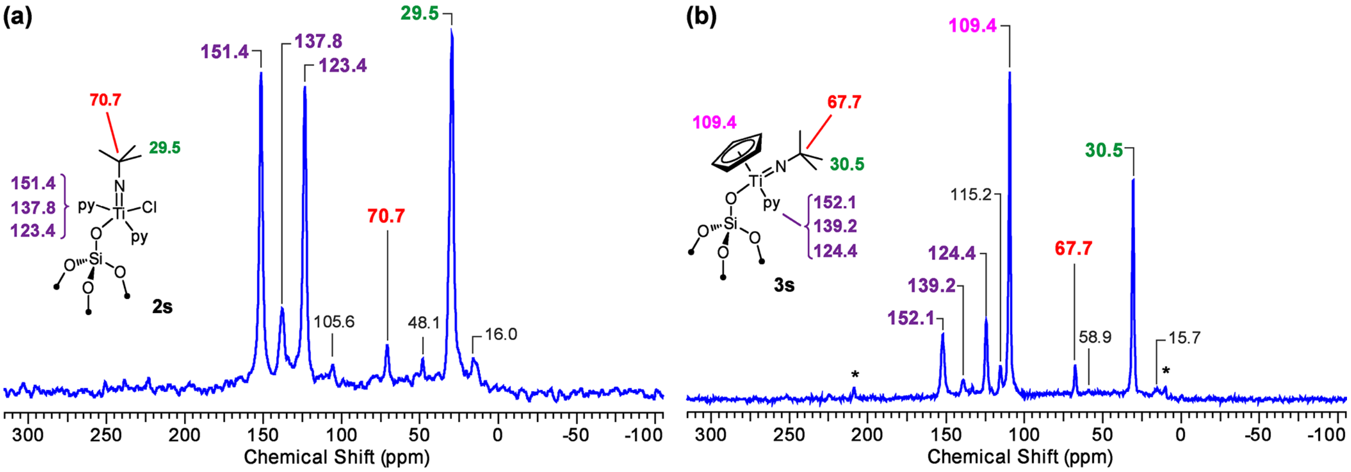
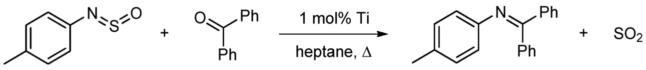


Figure 3. ^{13}C CP MAS solid-state NMR spectra of **2s** and **3s**.

Table 1. Activity of 1s−3s in Imidation of Benzophenone with TolNSO



catalyst	TOF$_{15\ \text{min}}$,[a] h^{-1}	$\tau_{1/2}$[b]
[(≡SiO)Ti(=N*t*Bu)(Me$_2$Pyr)(py)$_2$] (**1s**)	385(18)	5 min
[(≡SiO)Ti(=N*t*Bu)Cl(py)$_2$] (**2s**)	53(9)	1−2 h
[(≡SiO)Ti(=N*t*Bu)Cp(py)] (**3s**)	258(11)	10 min

[a] TOF averaged for the first 15 min of the reaction (standard deviations are given in parentheses). [b] Half-conversion time.

on Ti has a very strong influence on the catalytic performance and (ii) electron-donating ligands generally favor the activity. Me$_2$Pyr and Cp complexes **1s** and **3s** are both very efficient catalysts, while **2s** bearing a chloride, despite being an isostructural analogue of **1s**, displays almost 1 order of magnitude lower activity. It is worth noting, however, that Cp derivative **3s** is somewhat less active than **1s**, the difference being even more pronounced when the more sterically demanding MesNSO (Mes = 2,4,6-Me$_3$C$_6$H$_2$) is used instead of TolNSO. In this case catalysts **1s** and **3s** give TOF$_{15\ \text{min}}$ values of ca. 80 vs 30 h^{-1} and half-conversion times of 45 min vs 2 h, respectively.

While chloride is a very poorly donating ligand and η^5-Cp is a strong σ-/π-donor, η^1-Me$_2$Pyr is known to be a good σ-donor but a weak π-donor, and thus the overall electron-donating ability of these ligands can be ranked as follows: Cl < Me$_2$Pyr < Cp.[14,16] In this context the superior activity of the pyrrolyl catalyst **1s** is surprising, especially considering the fact that the preference for the electron-rich metal center in this reaction could be rationalized as a result of the imido nitrogen lone pair being in that case less involved in bonding with Ti and more localized on the nitrogen atom (this is also reflected in longer $d_{\text{Ti=N}}$, see above), which in turn makes the imido group more prone toward the nucleophilic attack on the ketone.[4c]

The difference between **1s** and **3s** may arise from different origins. First, it should be noted that, unlike **1s** and **2s** which are both 5-coordinated, **3s** is formally a 6-coordinated complex, and in addition the formal electron count gives 14e for **1s** and **2s**, while **3s** can be regarded as having 16e (the imido ligand is counted as an X$_2$L ligand). Thus, a direct comparison between **1s** and **3s** may be ambiguous. Another factor that can play a role in catalysis is the potentially flexible hapticity of the pyrrolyl ring. However, a more likely explanation consists of the Me$_2$Pyr ligand being transformed under the reaction conditions. Indeed, the amide ligand bound to the oxophilic Ti atom is very reactive and susceptible to protonolysis and insertion reactions (which is also the reason for clean and selective grafting via this ligand), and therefore it is reasonable to expect that it may not stay intact in the presence of the reactive organic substrates. This is also in agreement with the preliminary DFT calculation results which show that when Me$_2$Pyr and N*t*Bu ligands are simultaneously present in the coordination sphere of Ti the HOMO is actually located on the pyrrolyl while the imido orbitals involved in catalysis lie lower in energy. Thus, it may appear that **1s** is only a precatalyst and the Me$_2$Pyr ligand cannot be directly placed on

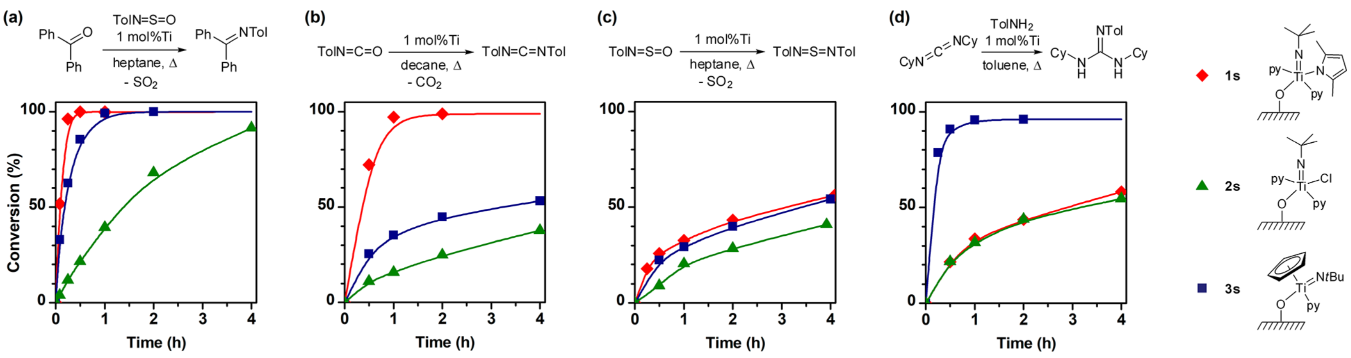
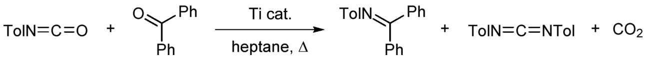


Figure 4. Catalytic performance of supported catalysts **1s**−**3s** in (a) imidation of benzophenone with TolNSO, (b) self-condensation of TolNCO, (c) self-condensation of TolNSO, and (d) guanylation reaction between DCC and TolNH$_2$. Lines are added to guide the eye.

the same scale as the more stable Cp and Cl, and its role during catalysis, as well as the origin of the high activity of **1s**, requires a more careful analysis. It should also be mentioned that the competition between cycloaddition reactions of the Ti═NR linkage and insertions into the reactive Ti−X bonds in related systems has been discussed in detail by Mountford.[17]

We were interested to evaluate the synthetic potential of using isocyanates instead of *N*-sulfinylamines under the same conditions. Isocyanates are well-known imidating agents for oxo complexes[18] (in this case the coproduct of the reaction is CO_2, while SO_2 is released in the reactions with *N*-sulfinylamines), and they have also been used in the catalytic imidation of carbonyl compounds.[3e,19] Surprisingly, we have found that when TolNCO is used under conditions identical with those employed for TolNSO only trace amounts of benzophenone imine product (1−2%) are detected after 1 h of reaction, and only 5−10% after 24 h, with any of the catalysts **1s**−**3s** (Table 2). It is worth noting that the same order of activity as in the case of *N*-sulfinylamines is observed (**1s** > **3s** > **2s**). Increasing the catalyst loading to 5 mol % gives 70% conversion into imine after 24 h with the most active catalyst **1s**. Thus, *N*-sulfinylamines are strikingly more reactive imidating agents in this transformation in comparison to the corresponding isocyanates, which implies that at least in the case of isocyanates the limiting step of the catalytic cycle (Scheme 1) is the imidation of M═O rather than an imido-transfer to ketone. This result correlates with the data on the stoichiometric imidation of transition-metal oxo complexes using *N*-sulfinylamines and isocyanates,[18,20] the latter typically requiring higher temperatures and longer reaction times.

Table 2. Activity of 1s−3s in Imidation of Benzophenone with TolNCO

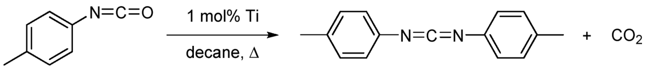


		conversion after 24 h, %[a]	
catalyst	Ti, mol %	imine	carbodiimide
1s	5	70	15
1s	1	9	16
2s	1	4	2
3s	1	5	6

[a] Conversions into imine and carbodiimide products. These tests were performed only once, and thus no standard deviations are given. Note that the accuracy of GC data at low conversions is rather low.

In the course of the reaction we have also detected the formation of small amounts of the carbodiimide TolNCNTol (15% after 24 h with 5 mol % of **1s**, Table 2). This product likely results from a concurrent oxo/imido heterometathesis process where 1 equiv of RNCO acts as an imidating agent and another 1 equiv as an oxo component (although alternative mechanisms have also been proposed[21]). This reaction was reported for several transition-metal oxo and imido complexes[3g,h,22] and typically requires harsh reaction conditions—heating at temperatures as high as 140−190 °C (sometimes in neat isocyanate). We have tested the catalysts **1s**−**3s** in the self-condensation of TolNCO. The reaction in refluxing toluene (110 °C) is very slow and reaches ca. 90% conversion within 4 days when 1 mol % of **1s** is used as a catalyst. Increasing the temperature to 174 °C (reflux in *n*-decane) results in much faster reaction—quantitative conversion is reached within 1 h with catalyst **1s** (Figure 4b). Again the same order of activity as in the imidation of benzophenone is observed: **1s** > **3s** > **2s** (Table 3); however, in this case **1s** displays significantly better performance than **3s**.

Table 3. Activity of 1s−3s in Condensation of TolNCO



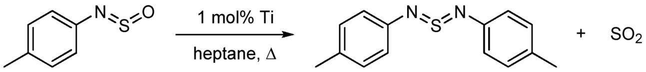
catalyst	$TOF_{30\ min}$,[a] h^{-1}	$\tau_{1/2}$[b]
$[(\equiv SiO)Ti(=N\textit{t}Bu)(Me_2Pyr)(py)_2]$ (**1s**)	144(17)	<30 min
$[(\equiv SiO)Ti(=N\textit{t}Bu)Cl(py)_2]$ (**2s**)	22(13)	>4 h
$[(\equiv SiO)Ti(=N\textit{t}Bu)Cp(py)]$ (**3s**)	44(17)	2−4 h

[a] TOF averaged for the first 30 min of the reaction (standard deviations are given in parentheses). [b] Half-conversion time.

We have also tested the catalyst **1s** under conditions similar to those reported by Sundermeyer for the homogeneous phtalocyanine-supported Ti oxo complex [(Pc)Ti(═O)], which fully converts TolNCO into carbodiimide at 190 °C and 0.3 mol % catalyst loading within 6 days.[3g] The reaction with 0.3 mol % of **1s** is complete after reflux overnight at 174 °C (in fact, ca. 80% conversion is achieved already after 1.5 h), and thus silica-supported catalyst **1s** displays even better performance than the homogeneous catalyst. It should be noted, however, that all the reported transition-metal-based systems are dramatically inferior to the well-known phospholene oxide catalysts,[23] and thus, despite being intriguing, this reaction at the moment is mainly interesting from a mechanistic point of view. In this respect, important for us is the correlation between the difficulty of self-condensation of isocyanates and their poor reactivity as imidating agents for ketones and other oxo substrates.

A similar transformation can be observed for *N*-sulfinylamines in the absence of other oxo substrate: i.e., their self-condensation into sulfurdiimines with liberation of SO_2 (Table 4), as has been demonstrated before for Mo- and Ta-based catalysts.[3c,5] Similarly to the imidation of benzophenone, self-condensation proceeds much more easily in the case of *N*-sulfinylamines (the reactions with 1 mol % of Ti are relatively fast already at 98 °C). The results for **1s**−**3s** are shown in Table 4 and Figure 4c. The difference between the catalysts is not strongly pronounced in this case; however, the same order of activity is observed, with catalysts **1s** and **3s** being slightly more active than **2s**.

Table 4. Activity of 1s−3s in Condensation of TolNSO



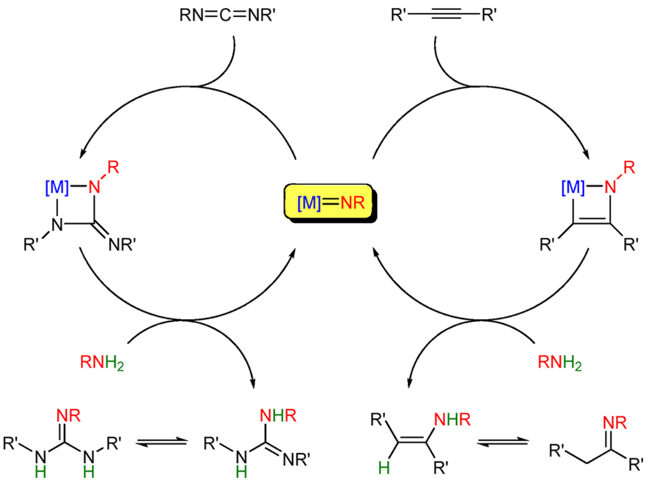
catalyst	$TOF_{30\ min}$,[a] h^{-1}	$\tau_{1/2}$[b]
$[(\equiv SiO)Ti(=N\textit{t}Bu)(Me_2Pyr)(py)_2]$ (**1s**)	49(4)	4 h
$[(\equiv SiO)Ti(=N\textit{t}Bu)Cl(py)_2]$ (**2s**)	22(5)	4−8 h
$[(\equiv SiO)Ti(=N\textit{t}Bu)Cp(py)]$ (**3s**)	44(8)	4 h

[a] TOF averaged for the first 30 min of the reaction (standard deviations are given in parentheses). [b] Half-conversion time.

Cycloaddition reactions between early-transition-metal imido complexes and unsaturated compounds serve as entry points into many other catalytic cycles besides oxo/imido heterometathesis. In particular, cycloaddition with alkynes is a key elementary step in alkyne hydroamination,[14a,24] carboamination,[25] and iminoamination,[26] as well as in pyrrole synthesis via [2 + 2 + 1] coupling of alkynes with azo compounds[27] and organic azides.[28] Ti-catalyzed hydroamination of alkynes

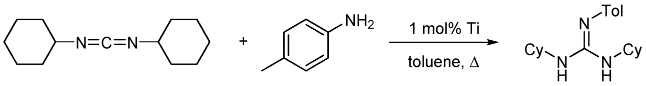
(Scheme 3) has been extensively studied by many groups, especially by Odom,[14a,26] who has also recently investigated the silica-supported systems.[29] We have preliminarily tested the grafted catalysts **1s**−**3s** in the hydroamination of internal alkynes (which are known to be significantly more challenging substrates than the terminal alkynes) with *p*-toluidine ($TolNH_2$) at 5 mol % Ti loading in boiling toluene (110 °C). So far we have not been able to observe activity with 4-octyne; however, moderate activity is found in the hydroamination of diphenylacetylene. According to the preliminary data the catalyst **3s** displays the best performance (ca. 90% conversion in 24 h), while **1s** is less active (ca. 70% after 24 h) and **2s** is almost inactive under these conditions. This result is in line with Bergman's finding[30] that $[Ti({=}NAr)Cp(NHAr)(py)]$ (Ar = 2,6-$Me_2C_6H_4$), which is structurally very similar to the surface complex **3s**, efficiently catalyzes the hydroamination of diphenylacetylene, although the activity of **3s** is significantly lower. On the other hand, the only reported heterogeneous Ti system operates under much harsher conditions,[29] and thus this result is worth studying in more detail.

Scheme 3. Alkyne and Carbodiimide Hydroamination Catalytic Cycles



Hydroamination of carbodiimides (also referred to as "guanylation of amines with carbodiimides") catalyzed by Ti imido complexes was first reported by Richeson in 2003[31] and proposed to follow a mechanism similar to that of hydroamination of alkynes (Scheme 3). Many catalytic systems have been tested since that time,[32] including one report of a silica-supported Ti catalyst by Odom.[29a] Using the reaction between equimolar amounts of dicyclohexylcarbodiimide (DCC) and $TolNH_2$ in boiling toluene (110 °C) at 1 mol % catalyst loading, we have found that heterogeneous catalysts **1s**−**3s** display good activities in this transformation (Table 5 and Figure 4d). Especially noteworthy is the catalyst **3s**, which reaches almost quantitative conversion within 30 min. Interestingly, the performances of the catalysts **1s** and **2s** are nearly identical. This result could be explained on the basis of the fact that both pyrrolyl and chloride ligands could be expected to be substituted in the presence of excess aniline, leading to formally the same catalytic species and hence close activities. In contrast, the Cp ligand of **3s** is more likely to stay intact during the reaction—this is another typical example in organometallic chemistry when the ubiquitous cyclopentadienyl ligand provides a suitable framework for productive and stable catalysis.

Table 5. Activity of 1s−3s in Catalytic Guanylation



catalyst	$TOF_{30\ min}$,[a] h^{-1}	$\tau_{1/2}$[b]
$[(\equiv SiO)Ti({=}N\textit{t}Bu)(Me_2Pyr)(py)_2]$ (**1s**)	46(5)	2−4 h
$[(\equiv SiO)Ti({=}N\textit{t}Bu)Cl(py)_2]$ (**2s**)	48(7)	2−4 h
$[(\equiv SiO)Ti({=}N\textit{t}Bu)Cp(py)]$ (**3s**)	182(8)	<15 min

[a] TOF averaged for the first 30 min of the reaction (standard deviations are given in parentheses). [b] Half-conversion time.

■ CONCLUSION

We have prepared and characterized two new well-defined silica-supported Ti imido complexes with the Ti atom in different ligand environments. Although we have so far not been able to find a catalyst that would exceed the performance of the most efficient previously reported oxo/imido heterometathesis catalyst **1s**, we have identified the important trends in activity that will guide further catalyst development. In particular we have shown that (i) the performance of structurally similar catalysts may vary drastically depending on the nature of the ancillary ligands, (ii) an electron-donating environment tends to generally favor the activity, and (iii) the same order of activity is observed for different oxo/imido heterometathesis reactions (**1s** > **3s** > **2s**), which gives an additional proof that all of these reactions follow the same general mechanism. We have also shown that silica-supported Ti imido complexes are active in other catalytic imido-transfer reactions typical for molecular imido complexes, in particular the hydroamination of alkynes and carbodiimides; a more detailed study of these reactions is underway.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. All glassware was dried in an oven at 130 °C for at least 2 h prior to use. Solvents were distilled from Na/benzophenone (THF, Et_2O, toluene, C_6H_6, C_6D_6, pentane, heptane, decane) or CaH_2 (CH_2Cl_2, $CDCl_3$), degassed by three freeze−pump−thaw cycles, and stored over activated 3 Å MS. $TolNH_2$ and diphenylacetylene were sublimed under vacuum. DCC was dissolved in dry CH_2Cl_2, filtered, evaporated, and distilled under vacuum. TolNCO and 4-octyne were used as received. TolNSO was prepared by refluxing $TolNH_2$ in toluene with 1.1 equiv of $SOCl_2$ (Merck, "for synthesis" grade) overnight (or until the solid that initially formed fully dissolved), with subsequent evaporation of the solvent and vacuum distillation. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, ^3J 8.2, 2H), 7.22 (d, 2, 2H), 2.39 (s, 3H). Benzophenone was dried either by sublimation under vacuum (cooling the cold finger with tap water) or by treating its toluene solution with 3 Å MS with subsequent crystallization at low temperature (both procedures give close results in catalysis). Silica (Degussa Aerosil, 200 $m^2\ g^{-1}$) was compacted with distilled water, calcined at 500 °C under air overnight, and then treated at 700 °C under high vacuum (ca. 10^{-5} mbar) for 24 h (support referred to as $SiO_{2\text{-}700}$).[1c] The solution NMR spectra were recorded using Bruker Avance 400, Avance II 300, DRX 300, and DRX 500 spectrometers. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. ^1H chemical shifts were referenced relative to the (residual) solvent peak: $CDCl_3$ (^1H, 7.26; ^{13}C, 77.16), C_6D_6 (^1H, 7.16; ^{13}C, 128.06). Solid-state NMR spectra were recorded on a Bruker Avance III 400 spectrometer, using a 4 mm double-resonance probe. Chemical shifts were referenced externally to solid adamantane (^1H, 1.91; ^{13}C, 38.5 (CH_2)). Samples were loaded in 4 mm zirconia rotors inside the glovebox and tightly closed. Cross-polarization magic angle spinning

(CP MAS) type experiments were employed in order to acquire ^{13}C spectra at 10 kHz MAS, and ^{1}H decoupling was performed using the SPINAL64 sequence.[33] IR spectra of silica and grafted materials were recorded using a Bruker spectrometer placed in the glovebox, equipped with OPUS software. Samples were pressed into pellets inside the glovebox, and transmission spectra were measured in the region of 4000−400 cm^{-1}. GC/FID was performed using a Chromatec Crystal 5000.2 gas chromatograph equipped with a Restek RTX-35 column. Elemental analyses were performed in the Laboratories of Microanalysis of INEOS RAS and ETH Zürich. X-ray diffraction data were taken using an Oxford Diffraction Xcalibur S κ geometry diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). To prevent evaporation of cocrystallized solvent molecules, the crystals were coated with Paratone oil in the glovebox and the data were collected at 100 K. The cell parameters were obtained with intensities detected on three batches of five frames. The crystal−detector distance was 4.5 cm, and the narrow data were collected using 1° increments. Unique intensities detected on all frames using the Oxford Diffraction Red program were used to refine the values of the cell parameters. The structure was solved by direct methods using Olex2 1.2 with the SHELXTL-2012 package, and for all structures all atoms, including hydrogen atoms, were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on *F*.

[Ti(═N*t*Bu)Cl(Me$_2$Pyr)(py)$_2$] (2). To a solution of Ti(═N*t*Bu)-Cl$_2$(py)$_3$[13] (966 mg, 2.26 mmol) in THF (20 mL) was added a solution of NaMe$_2$Pyr (265 mg, 2.26 mmol) in THF (5 mL) at −35 °C, and the reaction mixture was stirred overnight at room temperature (alternatively, the starting materials can be mixed as solids and dissolved in cold THF; LiMe$_2$Pyr gives the same yields but note however that it is insoluble in THF). The solution turned from red to yellow-orange. The solvent was evaporated under vacuum, and the residue was extracted with toluene to give an orange solution. Toluene was evaporated, and the orange oily residue was triturated in heptane to give a yellow powder that was filtered, washed with fresh heptane, and dried under vacuum to give 746 mg (81%) of analytically pure product. The complex is insoluble in heptane, moderately soluble in Et$_2$O, and soluble in toluene and benzene. Large orange XRD-suitable crystals were obtained by diluting an Et$_2$O solution of the product with pentane (to ca. 1/1 Et$_2$O/pentane ratio) and cooling the solution to −35 °C overnight. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 8.88 (d, ^{3}J 4.9, 4H, *o*-C*H*$_{\text{py}}$), 6.74 (t, ^{3}J 7.6, 2H, *p*-C*H*$_{\text{py}}$), 6.50 (t, ^{3}J 6.6, 4H, *m*-C*H*$_{\text{py}}$), 6.45 (s, 1H, Me$_2$*Pyr*), 6.13 (s, 1H, Me$_2$*Pyr*), 3.12 (s, 3H, *Me*$_2$Pyr), 2.03 (s, 3H, *Me*$_2$Pyr), 1.06 (s, 9H, N*t*Bu). ^{13}C NMR (C$_6$D$_6$, 75 MHz): δ 151.8 (*o*-CH$_{\text{py}}$), 138.1 (*p*-CH$_{\text{py}}$), 133.8 (quat C$_{\text{Me2Pyr}}$), 129.6 (quat C$_{\text{Me2Pyr}}$), 124.2 (*m*-CH$_{\text{py}}$), 107.2 (CH$_{\text{Me2Pyr}}$), 106.8 (CH$_{\text{Me2Pyr}}$), 72.4 (NCMe$_3$), 31.3 (NC*Me*$_3$), 19.2 (*Me*$_2$Pyr), 14.8 (*Me*$_2$Pyr). Anal. Found (calcd for C$_{20}$H$_{27}$N$_4$ClTi): C, 59.21 (59.05); H, 6.79 (6.69); N, 13.63 (13.77). CCDC 1960613 contains the crystallographic data.

[Ti(═N*t*Bu)Cp(Me$_2$Pyr)(py)] (3). To a solution of Ti(═N*t*Bu)-Cl(Me$_2$Pyr)(py)$_2$ (**2**; 412 mg, 1.01 mmol) in THF (10 mL) was added a solution of CpNa (90 mg, 1.0 mmol) in THF (5 mL) at −35 °C, and the reaction mixture was stirred overnight at room temperature. The solution turned from orange to red. The solvent was evaporated under vacuum, and the residue was extracted with toluene to give a dark red solution. The solution was concentrated and cooled to −35 °C to give red crystals that were decanted, washed with pentane, and dried under vacuum. Yield: 221 mg (61%). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 8.39 (d, ^{3}J 4.9, 2H, *o*-C*H*$_{\text{py}}$), 6.64 (t, ^{3}J 7.6, 1H, *p*-C*H*$_{\text{py}}$), 6.41 (s, 2H, Me$_2$*Pyr*), 6.27 (t+s, 2H *m*-C*H*$_{\text{py}}$, + 5H C$_5$*H*$_5$), 2.34 (s, 6H, *Me*$_2$Pyr), 1.02 (s, 9H, N*t*Bu). ^{13}C NMR (C$_6$D$_6$, 125 MHz): δ 151.1 (*o*-CH$_{\text{py}}$), 134.5 (quat C$_{\text{Me2Pyr}}$), 134.3 (*p*-CH$_{\text{py}}$), 124.1 (*m*-CH$_{\text{py}}$), 110.5 (C$_5$H$_5$), 107.5 (CH$_{\text{Me2Pyr}}$), 68.3 (NCMe$_3$), 32.0 (NC*Me*$_3$), 19.2 (*Me*$_2$Pyr) (chemical shift of quat C$_{\text{Me2Pyr}}$ was extracted from HMBC spectrum). Anal. Found (calcd for C$_{20}$H$_{27}$N$_3$Ti): C, 67.35 (67.23); H, 7.58 (7.62); N, 11.65 (11.76). CCDC 1960614 contains the crystallographic data.

[(≡SiO)Ti(═N*t*Bu)Cl(py)$_2$] (2s). An orange benzene solution of Ti(═N*t*Bu)Cl(Me$_2$Pyr)(py)$_2$ (**2**; 73 mg, 0.18 mmol) was added to a suspension of SiO$_{2\text{-}700}$ (694 mg) in benzene at room temperature. The suspension was slowly stirred overnight while silica became orange and the solution colorless. The solid was separated by decantation and washed several times with fresh benzene. The resulting solid was dried under high vacuum (ca. 10^{-5} mbar) for 2 h to afford 720 mg of yellow powder. Filtrate solutions and volatiles trapped upon drying were collected and analyzed by ^{1}H NMR spectroscopy in C$_6$D$_6$ using ferrocene as an internal standard, indicating that 0.15 mmol of Me$_2$PyrH was released upon grafting (0.82 equiv/Ti). Elemental analysis (wt %): Ti 1.1% (0.23 mmol Ti g^{-1}), C 3.93%, H 0.75%, N 1.11%, Cl 0.85%; corresponding to 14.2 C/Ti, 32.6 H/Ti, 3.4 N/Ti, and 1.0 Cl/Ti (expected Ti/N/C/H/Cl = 1/3/14/19/1).

[(≡SiO)Ti(═N*t*Bu)Cp(py)] (3s). A red benzene solution of Ti(═N*t*Bu)Cp(Me$_2$Pyr)(py) (**3**; 78 mg, 0.22 mmol) was added to a suspension of SiO$_{2\text{-}700}$ (846 mg) in benzene at room temperature. The suspension was slowly stirred overnight while silica became dark red and the solution colorless. The solid was separated by decantation and washed several times with fresh benzene. The resulting solid was dried under high vacuum (ca. 10^{-5} mbar) for 2 h to afford 877 mg of an orange powder. Filtrate solutions and volatiles trapped upon drying were collected and analyzed by ^{1}H NMR spectroscopy in C$_6$D$_6$ using ferrocene as an internal standard, indicating that 0.20 mmol of Me$_2$PyrH was released upon grafting (0.92 equiv/Ti). Elemental analysis (wt %): Ti 1.1% (0.23 mmol Ti g^{-1}), C 4.08%, H 0.57%, N 0.86%; corresponding to 14.8 C/Ti, 24.8 H/Ti, and 2.7 N/Ti (expected Ti/N/C/H = 1/2/14/19).

Catalytic Studies. Stock solutions of the substrates (ca. 0.15 M) and C$_6$Me$_6$ (internal standard) in dry solvents were prepared and stored under argon. A catalyst (typically 20−30 mg) was placed in a double-neck Schlenk flask equipped with a backflow condenser at one neck and a septum for taking aliquots at the second neck. The required volume of the solution was added to the catalyst, the flask was immediately immersed in a preheated oil bath, and the reaction was carried out under reflux. Aliquots of the reaction mixture were taken over the course of the reaction and analyzed with GC. The conversions of the reagents were determined from their consumption with respect to the internal standard; the conversions into products were calculated using calibrations of the isolated products versus internal standard and usually matched well with the reagent conversions (no calibration was performed for alkyne hydroamination, and only consumption of the reagents was monitored in this case). The TON and TOF were calculated with respect to the total amount of the metal in the catalyst determined by elemental analysis. Each test was repeated several times (TOFs reported in Tables 1−5 are the average values, half-conversion times are given as ranges). For more details see ref 6. Ph$_2$C═NTol and TolN═S═NTol were prepared in our previous work.[5] TolN═C═NTol[34] was isolated as a pale yellow liquid in 83% yield after distillation under vacuum from the experiment with 0.3 mol % catalyst **1s** (reflux in *n*-decane overnight). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.13 (d, ^{3}J 8.2, 4H), 7.08 (d, 4H), 2.34 (s, 6H). Guanidine (NHCy)$_2$C(═NTol)[35] was isolated as a white powder by crystallization from toluene in 79% yield from one of the catalytic runs with 1 mol % catalyst **3s**: mp 153 °C (lit. mp 157−158 °C). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.04 (d, ^{3}J 8.0, 2H), 6.74 (d, 2H), 3.63 (br s, 2H), 3.40 (br s, 2H), 2.27 (s, 3H), 2.01−1.96 (m, 4H), 1.70−1.57 (m, 6H), 1.39−1.30 (m, 4H), 1.17−1.05 (m, 6H). The identity of the diphenylacetylene hydroamination product was confirmed using ESI-MS (MH^{+} calcd 286.1590, found 286.1588).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00779.

IR and NMR spectra (PDF)

Accession Codes

CCDC 1960613−1960614 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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