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Highly Active Dinuclear Titanium(IV) Complexes for the Catalytic Formation of a Carbon−Heteroatom Bond

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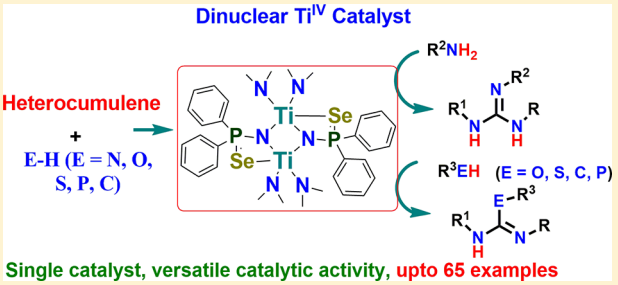
Supporting Information

ABSTRACT: A series of mononuclear titanium(IV) complexes with the general composition κ^3-[R{$NHPh_2P(X)$}$_2$Ti$(NMe_2)_2$] [R = C_6H_4, X = Se (**3b**); R = *trans*-C_6H_{10}, X = S (**4a**), Se (**4b**)] and [{κ^2-$N(PPh_2Se)_2$}$_2$Ti$(NMe_2)_2$] (**6b**) and two dinuclear titanium(IV) complexes, [C_6H_4{$(NPh_2PS)(N)$}Ti(NMe_2)]$_2$ (**3c**) and [{κ^2-$N(PPh_2Se)$}Ti$(NMe_2)_2$]$_2$ (**6c**), are reported. Dinuclear titanium(IV) complex **6c** acts as an efficient catalyst for the chemoselective addition of an E−H bond (E = N, O, S, P, C) to heterocumulenes under mild conditions. The catalytic addition of aliphatic and aromatic amines, alcohol, thiol, phosphine oxide, and acetylene to the carbodiimides afforded the corresponding hydroelemented products in high yield at mild conditions with a broader substrate scope. The catalytic efficiency of the dinuclear complex depends on the cooperative effect of the Ti^{IV} ions, the systematic variation of the intermetallic distance, and the ligand's steric properties of the complex, which enhances the reaction rate. Most interestingly, this is the first example of catalytic insertion of various E−H bonds into the carbodiimides using a single-site catalyst because only the titanium-mediated insertion of E−H into a C═N unsaturated bond is reported to date. The amine and alcohol insertion reaction with the carbodiimides showed first-order kinetics with respect to the titanium(IV) catalyst as well as substrates. A most plausible mechanism for hydroelementation reaction is also proposed, based on the spectroscopic data of the controlled reaction, a time-course study, and the Hammett plot.



INTRODUCTION

The catalytic hydroelementation reaction, usually achieved by the addition of E−H moieties (E = N, O, S, P, C, Si, B) to unsaturated bonds, represents an atom-economical reaction in the functionalization of unsaturated compounds. This process has experienced a phenomenal acceleration in research activity over the past 2 decades.[1] Some representative results of hydroelementation for the construction of C−heteroatom bonds consist of hydroamination,[2] hydrothiolation,[3] hydrosilylation,[4] alkyne oligomerizations,[5] hydroboration[6] reactions, and so on. These types of catalytic processes are at the receiving end of intense interest because they involve atom-economical routes for the synthesis of various families of organic molecules, and this renders them attractive to both green chemistry and low-cost industrial processes. However, this reaction cannot proceed without the presence of a suitable catalyst to overcome the electrostatic repulsion between electron-rich π systems such as alkynes, alkenes, carbodiimides, and Lewis bases such as amines (hydroamination), phosphins (hydrophosphination) or phosphine oxides (hydrophosphorylation), alcohol (hydroalkoxylation), thiols (hydrothiolation), and so on. Moreover, this reaction is entropically not favored. Further, in the absence of a catalyst, limited substrate scopes such as hydroamination of activated alkenes via a catalytic intramolecular addition reaction and hydrophosphorylation of alkenes have been reported.[7] Hydroelementation reactions of alkenes and alkynes are very well reported and have been studied using a wide range of transition-metal, lanthanide, actinide, and alkali-metal catalysts.[8−11] However, until now, hydroelementation of heterocumulenes has scarcely been investigated using a suitable catalyst or metal precursors. Hydroelementation of heterocumulenes, which affords the guanidine, phosphaguanidine, propargylamine, and thiourea products in a straightforward manner, has found considerable utility as ligands in coordination compounds,[12] medicinal applications,[13] and synthons for challenging organic transformations.[14] Recently, Eisen et al. reported the actinide-mediated insertion of E−H bonds (E = N, P, O, S) into various heterocumulenes including carbodiimides, isocyanates, and isothiocyanates (Figure 1).[15−18] Similarly, Hill et al. have reported that the magnesium alkyl complex [CH{C(Me)-NDipp}$_2$}Mg^{n}Bu] (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) is an effective precatalyst for the catalytic hydroboration of alkyl- and aryl-substituted carbodiimides with pinacolborane as well as the catalytic C−C bond formation reaction between alkynes and

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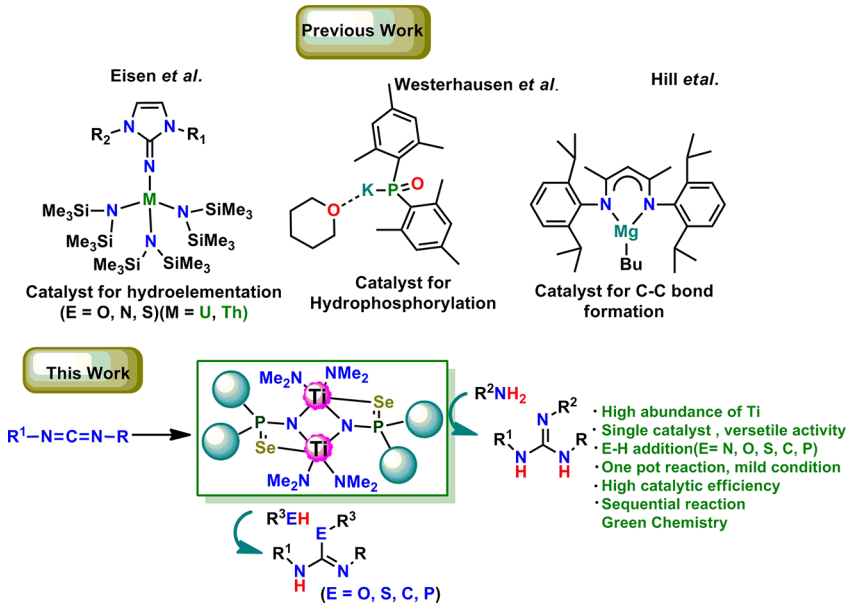

Figure 1. Selective examples of catalysts known for hydroelementation of heterocumulenes.

isocyanates to form bis(imidazolidine-2,4-diones) (Figure 1).[6,19] In addition, Westerhausen et al. have also recently described the use of potassium-mediated tetramers $[(thp)K(OPMes_2)]_4$ and $[(thf)_3\{K(OPMes_2)\}_4]$ for the hydrophosphorylation of heterocumulenes with diarylphosphine oxide and sulfide (Figure 1).[20] In all cases, the catalytic hydroelementation of heterocumulenes usually involves only two or four kinds of E−H nucleophiles (E = N, P, O, S) or heterocumulene substrates, which provide only a limited substrate scope.[21−23] Therefore, developing a single catalytic system that can perform versatile reactions such as the addition of E−H (E = N, O, S, P, C) moieties to heterocumulenes with a broader substrate scope is highly challenging. Nevertheless, it is interesting to develop catalysts that exhibit high tolerance toward heteroatoms and various functional groups that are able to catalyze diversified substrates.

In recent years, several researchers have developed a rich catalytic chemistry from the relatively inexpensive and earth-abundant group 4 metals in a variety of heterofunctionalisation, dehydrocoupling, and polymerization reactions.[24−31] Among the group 4 metals, titanium is the most abundant. Moreover, it is also an inexpensive and relatively less toxic metal, and its bioaffinity makes it suitable for innumerable applications in chemical synthesis compared to the more expensive and hazardous actinide and Ae metals.[24−31] Therefore, various research groups worldwide are working to develop a suitable titanium-metal-mediated catalyst that can efficiently catalyze hydroelementation for the construction of C−heteroatom bonds. Recently, Bergman and Mindiola et al. reported titanium-mediated hydroamination and C−H bond activation reactions of unsaturated bonds.[32] Similarly, Tonks, Odom, and Doya et al. also developed a titanium-mediated catalyst for carboamination, multicomponent, and hydrophosphination reactions.[33,34] In a continuation to this, our group also successfully synthesized a titanium-mediated catalyst of the bis(phosphinoselenoic amide) ligand $[\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}Ti(NMe_2)_2]$ and the imidazolin-2-iminato ligand $[(Im^{Dipp}N)Ti(NMe_2)_3]$ (ImN = imidazolin-2-iminato; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) for the catalytic hydroamination of various heterocumulenes,[35,36] but the scope of these precatalysts is very limited. In this context, we wanted to design a new class of ligands that can preferably stabilize two Ti ions simultaneously to realize a dinuclear titanium(IV) complex, where the structure-bonding relationship of such complexes can provide a better understanding of the efficiency of the catalytic process. Here, we report the synthesis and structural details of a series of mononuclear titanium(IV) complexes with the general composition κ^3-$[R\{NHPh_2P(X)\}_2Ti(NMe_2)_2]$ [R = C_6H_4, X = Se (**3b**); R = *trans*-C_6H_{10}, X = S (**4a**), Se (**4b**)] and $[\{\kappa^2$-$N(PPh_2Se)_2\}_2Ti(NMe_2)_2]$ (**6b**) along with dinuclear titanium(IV) complexes κ^3-$[C_6H_4\{(NPh_2PS)(N)\}Ti(NMe_2)]_2$ (**3c**) and $[\{\kappa^2$-$N(PPh_2Se)\}Ti(NMe_2)_2]_2$ (**6c**). We also describe a general and efficient protocol for the catalytic insertion of E−H bonds (E = N, O, S, P, C) into heterocumulenes with a broader substrate scope using the dinuclear titanium(IV) catalyst **6c** to yield a chemoselective product.

RESULTS AND DISCUSSION

Preparation of Titanium(IV) Complexes. Tetrakis(dimethylamido)titanium(IV) $[Ti(NMe_2)_4]$ was made to react with 1 equiv of the protic ligand $[R\{NHPh_2P(X)\}_2]$ [R = C_6H_4, X = S (**1a**), Se (**1b**); R = C_6H_{10}, X = S (**2a**), Se (**2b**)][37−39] in toluene at ambient temperature for 3 h to afford the corresponding titanium complexes κ^3-$[R\{NP(X)Ph_2\}_2Ti(NMe_2)_2]$ [R = C_6H_4, X = Se (**3b**); R = C_6H_{10}, X = S (**4a**), Se (**4b**)] in good yield (Scheme 1) as yellow solids. The solid-state structure of the titanium complex **4a** is already reported by Zhang et al.,[39] whereas the molecular structures of the other titanium(IV) complexes (**3b** and **4b**) in their solid state were confirmed by single-crystal X-ray diffraction analysis. In a similar fashion, the reaction between the diselenoimidodiphosphine ligand $[HN(PPh_2Se)_2\}_2]$ (**5b**) and $[Ti(NMe_2)_4]$ in a 2:1 molar ratio at ambient temperature gave the corresponding titanium complex $[\{\kappa^2$-$N(PPh_2Se)_2\}_2Ti(NMe_2)_2]$ (**6b**; Scheme 2). All of the titanium complexes (**3b**, **4a**, **4b**, and **6b**) exhibited good solubility in common organic solvents such as tetrahydrofuran and toluene and were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and combustion

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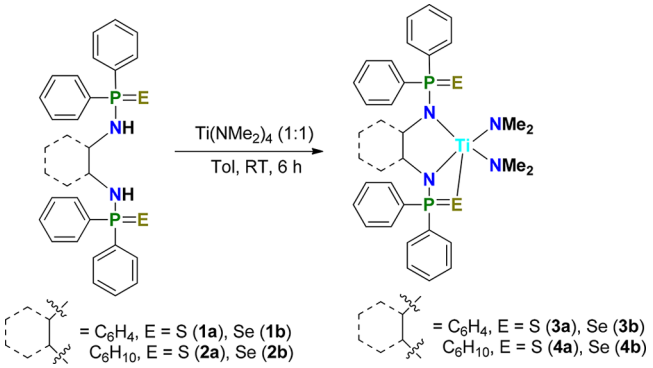
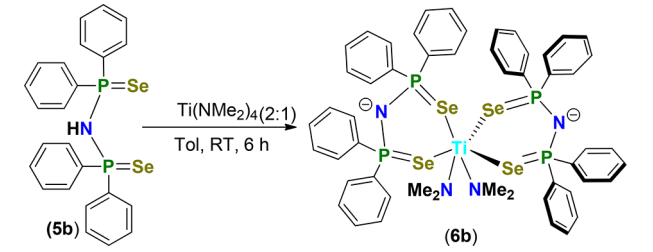
Scheme 1. Synthesis of Titanium(IV) Complexes 3a,3b, 4a, and 4b



Scheme 2. Synthesis of the Titanium(IV) Complex 6b from 5b



analysis (Figures FS5 and FS16). In the ^{31}P NMR spectra of complexes **3b** and **4b**, only one signal at 59.7 and 73.4 ppm was observed in each case along with two satellite peaks (Figures FS9 and FS12), indicating that both the P atoms are chemically equivalent. This is due to the rapid exchange between two Se atoms, one of which is bonded with Ti and the rate of exchange is faster than the NMR spectroscopy time scales. This kind of dynamic process is quite common in phosphorus chemistry and well reported in the literature.[36]

The molecular structures of **3b** and **4b** confirm the attachment of ligands **1b** and **2b** to a Ti ion in each case. Complex **3b** crystallizes in the monoclinic space group $P2_1/c$, with eight molecules in the unit cell. However, the analogous complex **4b** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$, with two molecules in the unit cell. Complex **6b** crystallizes in the monoclinic space group $C2/c$, with four molecules of **6b** and one toluene molecule in the unit cell. The details of the structural parameters are given in Table TS1. The solid-state structures of complexes **3b** and **4b** are given in Figures 2 and 3, respectively, and that of complex **6b** is given in Figure FS1. In both complexes **3b** and **4b**, the coordination polyhedron is formed by the dianionic ligand $-[R\{NPh_2P(Se)\}_2]^{2-}$ [R = C_6H_4 (**3b**), *trans*-C_6H_{10} (**4b**)] and two $-NMe_2$ groups to provide the metal-ion 5-fold coordination. Ligands **1b** and **2b** are bonded to the Ti metal ion through the chelation of two amido N atoms and one Se atoms attached to the P atoms. However, in complex **6b**, the Ti^{IV} ion adopts 6-fold coordination through the attachment of four Se atoms from two monoanionic *P*,*P*-diphenylphosphinoselenoic amido ligands $[N(PPh_2Se)_2]^-$ and two $-NMe_2$ groups, which are attached to the Ti atom cis to each other (Figure FS1).

When the time for the reaction between $[Ti(NMe_2)_4]$ and **1a** in a 1:1 molar ratio in toluene was extended to 12 h at ambient temperature, dinuclear titanium(IV) complex **3c** was obtained. A similar dinuclear complex of the molecular

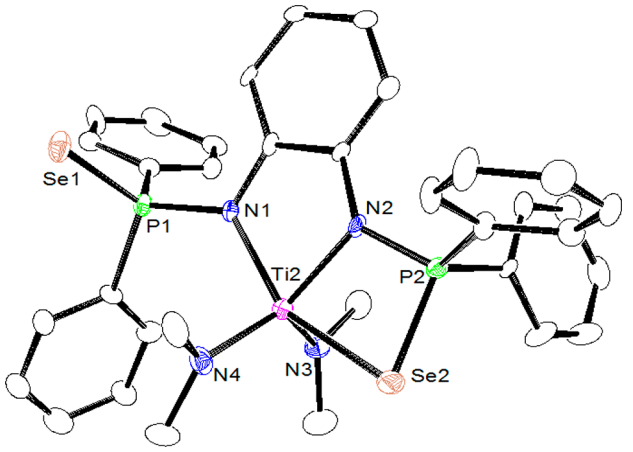


Figure 2. Molecular solid-state structure of **3b**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−Ti2 2.112(5), N2−P2 1.613(4), N2−Ti2 2.058(4), N3−Ti2 1.886(5), N4−Ti2 1.853(5), N5−P4 1.659(5), N5−Ti1 2.126(4), P1−Se1 2.1267(16), P2−Se2 2.1466(16), Ti2−Se2 2.6785(12); C1−N1−Ti2 116.8(3), P1−N1−Ti2 124.8(3), C6−N2−P2 132.7(4), C6−N2−Ti2 118.8(3), P2−N2−Ti2 106.4(2), N4−Ti2−N3 117.0(2), N4−Ti2−N2 130.7(2), N3−Ti2−N2 110.9(2), N4−Ti2−N1 102.6(2), N3−Ti2−N1 103.48(19), N2−Ti2−N1 75.80(17), N4−Ti2−Se2 90.06(15), N3−Ti2−Se2 95.82(15), N2−Ti2−Se2 74.19(13), N1−Ti2−Se2 148.55(12).

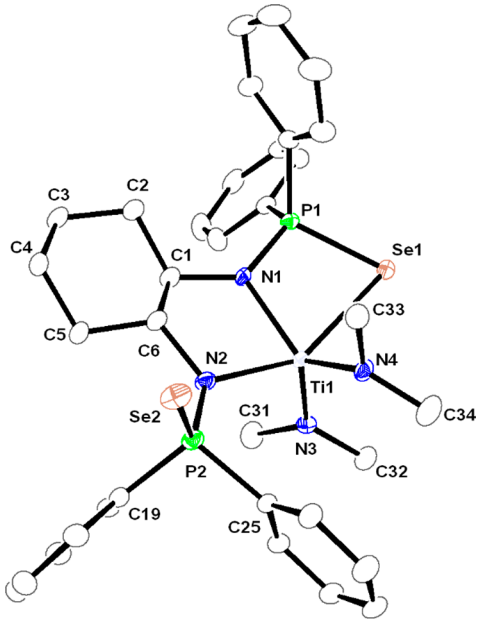


Figure 3. Molecular solid-state structure of **4b**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1−N4 1.872(4), Ti1−N3 1.877(4), Ti1−N1 2.043(4), Ti1−N2 2.096(4), Ti1−Se1 2.7202(10), Se1−P1 2.1527(13), Se2−P2 2.1316(15), P1−N1 1.612(4); N4−Ti1−N3 114.97(18), N4−Ti1−N1 128.82(17), N3−Ti1−N1 114.75(17), N4−Ti1−N2 101.13(17), N3−Ti1−N2 104.00(16), N1−Ti1−N2 77.95(14), N4−Ti1−Se1 88.98(13), N3−Ti1−Se1 96.89(12), N1−Ti1−Se1 73.81(10), N2−Ti1−Se1 150.00(10).

composition $[\{\kappa^2\text{-}N(PPh_2Se)\}Ti(NMe_2)_2]_2$ (**6c**) resulted in an analogous reaction of $[Ti(NMe_2)_4]$ and **5b** in a 1:1 molar ratio after 12 h of stirring (Scheme 3). Both complexes **3c** and **6c** were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and combustion analysis (Figures FS17−FS22),

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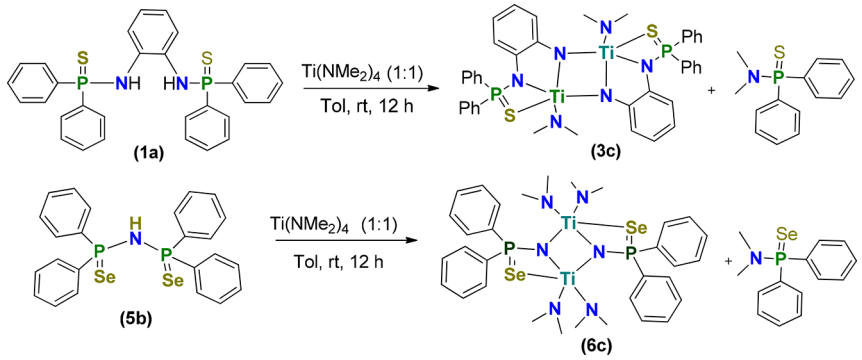
Scheme 3. Synthesis of the Titanium(IV) Complexes 3c and 6c



and their solid-state structures were confirmed by single-crystal X-ray diffraction analysis (see the Supporting Information). The molecular structures of complexes **3c** and **6c** in the solid state are given in Figures 4 and 5, respectively. Both complexes

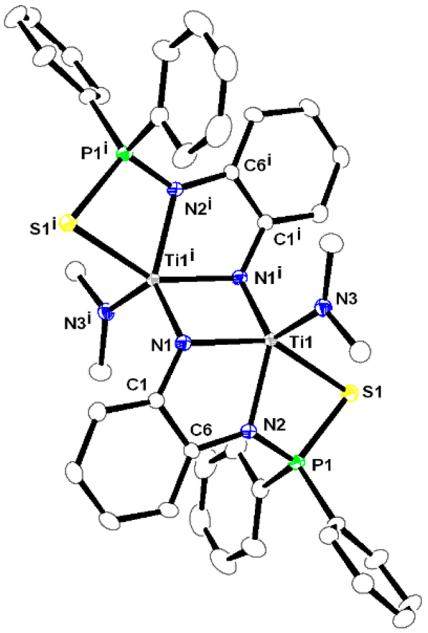


Figure 4. Molecular solid-state structure of **3c**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1−N1^{i} 1.8765(14), Ti1−N3 1.8913(15), Ti1−N1 2.0410(14), Ti1−N2 2.0714(13), Ti1−S1 2.5867(6); N1^{i}−Ti1−N3 110.04(6), N1^{i}−Ti1−N1 82.90(6), N3−Ti1−N1 108.42(6), N1^{i}−Ti1−N2 129.30(6), N3−Ti1−N2 120.18(6), N1−Ti1−N2, 75.61(5), N1^{i}−Ti1−S1 107.21(5), N3−Ti1−S1 98.81(5), N1−Ti1−S1 145.75(4), N2−Ti1−S1 72.85(4), P1−S1−Ti1 79.66(2).

3c and **6c** crystallize in the triclinic space group $P\bar{1}$; however, the unit cell of complex **3c** contains two toluene molecules as solvates. The details of the structural parameters are given in Table TS1. To the best of our knowledge, complexes **3c** and **6c** are the first examples of dinuclear titanium(IV) complexes with the *N*-(2-aminophenyl)-*P*,*P*-diphenylphosphinothioic amido and *P*,*P*-diphenylphosphinoselenoic amido ligands, respectively, where, in each case, [$Me_2NP(E)Ph_2$] (E = S or Se) is eliminated from the parent ligands **1a** and **5b** under the reaction conditions. The formation of titanium complexes **3c** and **6c** can be explained as shown in Scheme 1 in the Supporting Information.

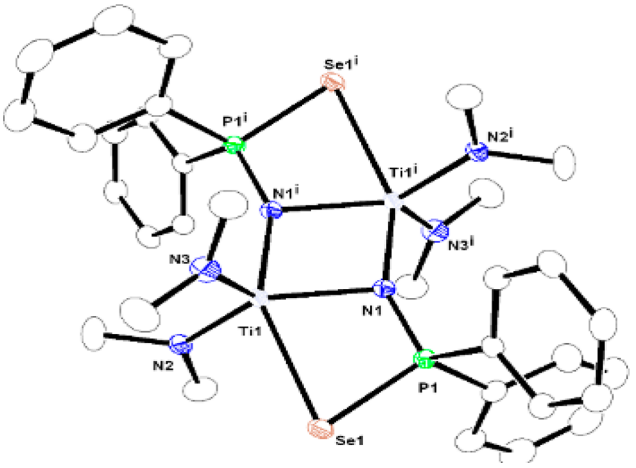


Figure 5. Molecular solid-state structure of **6c**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1−N3 1.889(4), Ti1−N2 1.904(3), Ti1−N1^{i} 1.970(3), Ti1−N1 2.044(3), Ti1−Se1 2.7654(9); N3−Ti1−N2 107.85(17) N3−Ti1−N1^{i} 100.63(15), N2−Ti1−N1^{i} 104.61(15), N3−Ti1−N1 116.62(15), N2−Ti1−N1 134.26(15), N1^{i}−Ti1−N1 77.97(15), N3−Ti1−Se1 99.35(12), N2−Ti1−Se1 88.03(11), N1^{i}−Ti1−Se1 151.65(10), N1−Ti1−Se1 75.17(9).

Catalytic Hydroelementation. All of the mono- and dinuclear titanium complexes **3a**−**3c**, **4a**, **4b**, **6b**, and **6c** were investigated as catalysts for the hydroelementation reaction. As a control experiment, a blank reaction was carried out at 65 °C for 24 h in the presence of only diisopropylcarbodiimide (DIC) and ethanol, which showed that ethyl *N*,*N*′-diisopropylcarbamimidate was not formed as a product. In order to determine the highest possible efficiency of the catalyst, the insertion of ethanol and aniline into DIC was monitored using ^{1}H NMR spectroscopy, showing the progress of the reaction as a function of DIC consumption, followed by the formation of ethyl *N*,*N*′-diisopropylcarbamimidate and guanidine, respectively (Table 1). After preliminary evaluation of the catalysts for hydroalkoxylation and hydroamination of DIC, we concluded that the dinuclear titanium(IV) catalysts (**3c** and **6c**) are substantially more efficient than their mononuclear analogues (**3a**, **3b**, **4a**,**4b**, and **6b**). A dinuclear catalytic system is significantly effective compared to the mononuclear catalyst of a similar structure because of cooperative interactions between the two metals and the substrate of the reaction.[40] Alternatively, a bimetallic catalyst design can be achieved by linking two discrete metal centers of proven catalytic efficiency through a covalently bound tether

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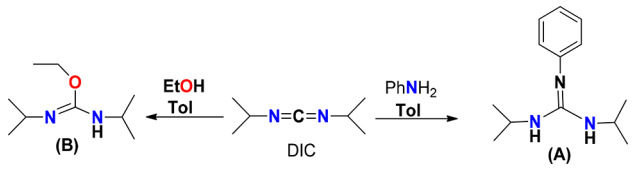
Table 1. Catalytic Addition of Ethanol and Aniline to DIC Promoted by Titanium(IV) Complexes To Give *N,N′*-Diisopropylcarbamimidate (B) and Guanidine (A), Respectively



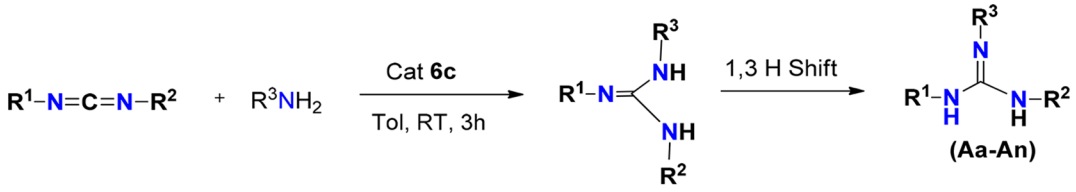
entry	catalyst	yield in hydroalkoxylation (%)	yield in hydroamination (%)
1	**3a**	50	65
2	**3b**	53	60
3	**4a**	42	52
4	**4b**	45	58
5	**6b**	55	64
6	**3c**	72	89
7	**6c**	95	97

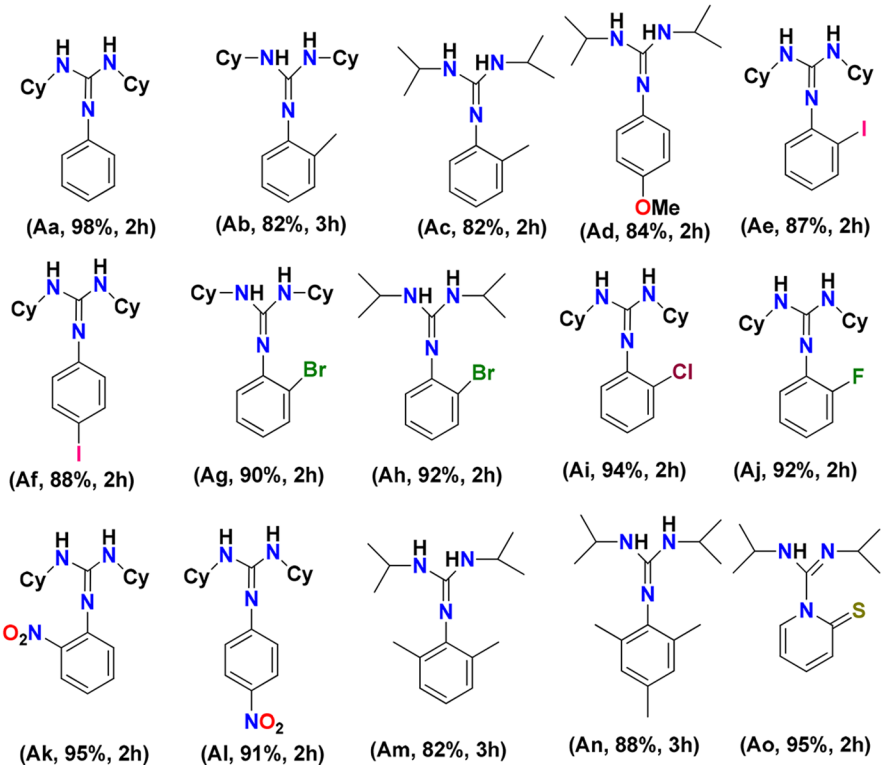
[a]Yields from ^{1}H NMR spectroscopy integrals using hexamethylbenzene as the internal standard. Yield calculated from the consumption of alcohols as well as amines. All reactions were carried out in toluene for 6 h.

that exhibits a remarkable catalytic cooperative effect, which is well reported in the literature.[41−47] In the case of μ-imidotitanium complexes that hold two Ti^{IV} metal centers at the proximal position, they are expected to not only assist electronic interaction between the two Ti metal centers via a μ-imido ligand but also show the cooperative effects of the two metal centers in catalytic transformation. Additionally, catalytic performances can also be fine-tuned by varying the nature of the ligand attached to the metal ions. Comparing the catalytic activity between **3c** and **6c**, we observed that complex **6c** is superior to **3c** as a catalyst for hydroalkoxylation and hydroamination under identical reaction conditions (Table 1, entries 6 and 7). The higher efficiency of **6c** can be attributed to the lesser crowded atmosphere around both the Ti^{IV} centers and the presence of two labile dimethylamido groups, which facilitate the addition reaction of incoming nucleophiles toward active metal centers compared to that of **3c**. Thus, complex **6c** was chosen as an effective precatalyst for the addition of the E−H bond (E = N, O, S, P, C) toward carbodiimides, and the results are summarized below.

All experiments presented here were performed in the presence of 1 equiv of heterocumulene and 1 equiv of a E−H moiety with 5 mol % catalyst loading. It was observed that the

Table 2. Insertion of Various Arylamines to Carbodiimides Using Complex 6c as the Catalyst[a]





[a]Reaction conditions: 4 mg of catalyst (0.005 mmol, ~0.5 mol %); cat./amine = 1/100; cat./carbodiimide = 1/100; 550 μL of $CDCl_3$; 25 °C. The yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

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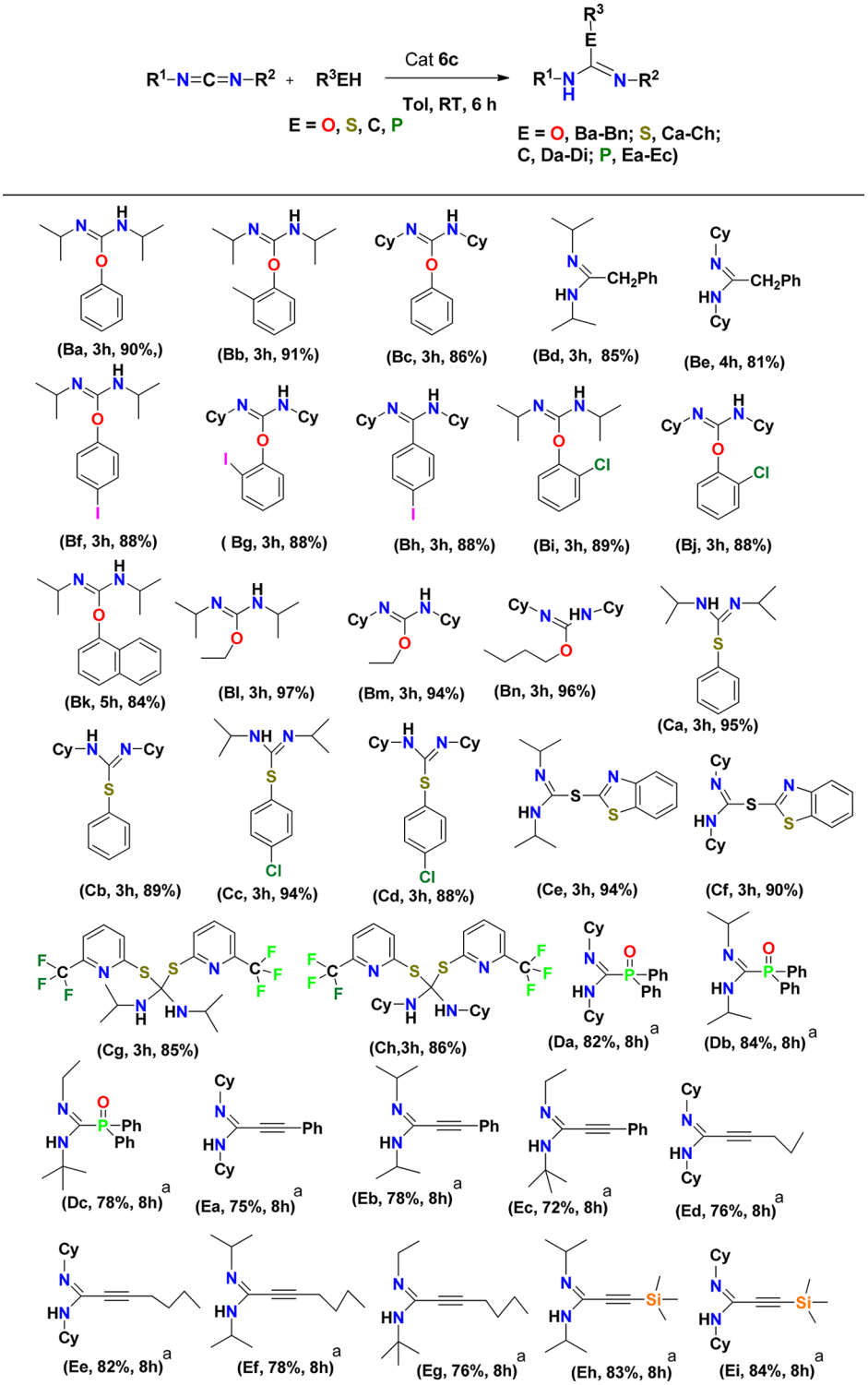
Table 3. Insertion of Various Alcohols, Thiols, Phosphine Oxides, and Terminal Alkynes into Carbodiimides Using 6c as the Catalyst[a]



[a]Reaction conditions: 4 mg of catalyst (0.005 mmol, ~0.5 mol %); cat./nucleophile = 1/100; cat./carbodiimide = 1/100; 550 μL of $CDCl_3$; at room temperature ([a]at 70 °C). The yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

addition of the E–H substrate affects the outcome of the insertion product. If E is a monoprotic nucleophile such as alcohol or thiol, the product (**B–E**) is formed as the sole insertion product. However, in the case of amine addition, where E corresponds to a diprotic nucleophile, isomerization of the initial product occurs, leading to guanidine derivatives (**Aa–An**) as the major products.

In the case of the hydroamination reaction, the arylamines with electron-donating groups such as 2-methylaniline and 4-methoxyaniline exhibited good conversion, affording the corresponding guanidines within 2 h at ambient temperature

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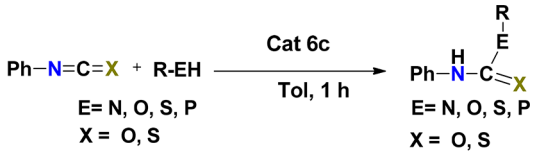
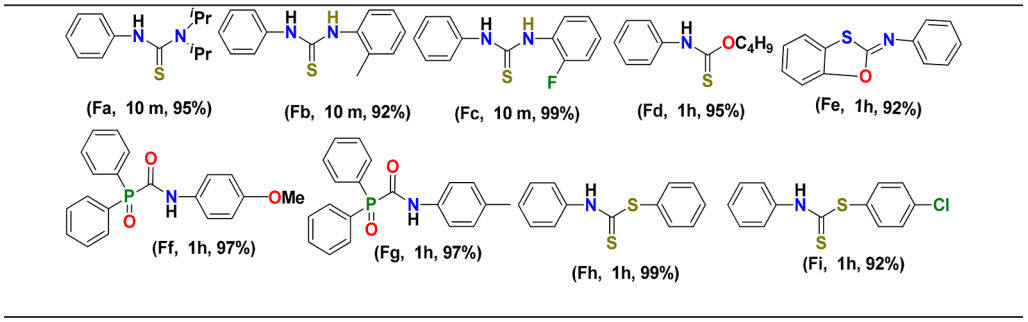
Table 4. Insertion of Amines, Alcohols, Thiols, and Phosphine Oxide to Phenyl Isothiocyanate and Isocyanate in the Presence of Catalyst 6c[a]





[a]Reaction conditions: 4 mg of catalyst (0.005 mmol, ~0.5 mol %); cat./nucleophile = 1/100; cat./carbodiimide = 1/100; 550 μL of $CDCl_3$; 25 °C. The yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

(**Ab**–**Ad**), whereas substituted arylamines with electron-withdrawing haloanilines such as iodo-, bromo-, chloro-, fluoro-, or nitroanilines exhibiting excellent yield (85–99%) afforded the desired guanidines within 2 h at room temperature (**Ae**–**Al**). In addition, substituted anilines with bulkier groups such as 2,6-$Me_2C_6H_3NH_2$ and 2,4,6-$Me_3C_6H_2NH_2$ could also be converted to the corresponding products (**Am** and **An**) up to 88%. The reaction of a substrate such as 2-mercaptopyridine, which consisted of amine (NH) and thiol (SH) groups as different nucleophiles in its two tautomeric forms, with an equimolar amount of DIC afforded *N*,*N*′-diisopropyl-2-thioxopyridine-1(2*H*)-carboximidamide (**Ao** in Table 2) in high yield, indicating that the reactivity of the amine group is greater compared to that of the thiols toward the carbodiimides. All of the products (**Aa**–**Ao**) were fully characterized with the help of NMR spectroscopy and mass spectrometry (MS) studies (Figures FS66–FS77), and the yields were calculated from isolated yields.

Further, catalytic hydroalkoxylation of the carbodiimides was performed with a number of alcohols. The reaction of three different carbodiimides and aryl, as well as aliphatic, alcohols catalyzed by complex **6c** afforded the corresponding chemoselective products (**Ba**–**Bn** in Table 3) in excellent yields (80–99%) within 3 h at room temperature (Figures FS78–FS99). DIC reacts faster with alcohols compared to dicyclohexylcarbodiimide (DCC) because of greater electron donation of the cyclohexyl groups than the isopropyl moieties (**Ba** and **Bc** in Table 3). The acidity and steric bulk of the respective alcohols played a crucial role in determining the reactivity of hydroalkoxylation. Aryl alcohols with electron-donating groups such as 2-methylphenol and benzyl alcohol afforded very good conversion (**Ba**–**Be** in Table 3), whereas aryl alcohols with electron-withdrawing iodo, chloro, and nitro groups could also be converted to the respective isourea in excellent yield (88–95%) within 3 h at 60 °C (**Bf**–**Bj** in Table 3). Although the reaction of β-naphthol with DCC did not yield any product, it reacted with DIC to give the expected product (**Bk** in Table 3) in higher conversion, presumably because of the smaller steric congestion imposed by the β-naphthol and isopropyl groups. The use of aliphatic alcohols, such as ethanol and 1-butanol, caused the rate of the hydroalkoxylation reaction with DIC to increase significantly (**Bl**–**Bn** in Table 3) compared to that of their aryl analogues.

Encouraged by the extraordinarily high catalytic activity of the dinuclear titanium(IV) complex **6c** and its greater tolerance of amine and alcohol functionality in guanylation and isourylation reactions, we extended the utilization of complex **6c** as a competent catalyst for the addition of a number of E–H bonds (E = S, P, C) to carbodiimides (Table 3) in order to explore the generality of catalyst **6c**. Thiophenol was first reacted with DIC in the presence of **6c** to afford a quantitative formation of thioguanidines (**Ca** and **Cb** in Table 3 and Figures FS100–FS103). Substituted arylthiols such as 4-chlorothiophenol and benzothiazole-2-thiol were also converted to the respective thioguanidines in excellent yields (85–98%) within 3 h at room temperature (**Cc**–**Cf** in Table 3 and Figures FS104–FS110). In contrast, 6-(trifluoromethyl)-pyridine-2-thiol yielded a bis-insertion product because of its high reactivity (**Cg** and **Ch** in Table 3 and Figures FS111–FS113) toward carbodiimides under identical reaction conditions. Thus, it can be said that the pyridyl group present in 6-(trifluoromethyl)pyridine-2-thiol exhibited no influence on hydrothiolation, indicating significant tolerance of the heterocyclic functionalities toward the dinuclear catalyst **6c**. Complex **6c** also proved to be a potent catalyst in hydrophosphorylation with use of the diphenylphosphine oxide [$Ph_2P(O)H$] and three carbodiimides. Diphenylphosphine oxide was smoothly converted to the corresponding phosphorylguanidine using catalyst **6c** in each case (**Da**–**Dc** in Table 3 and Figures FS113–FS120). Moreover, the presence of two resonance peaks in the ^{31}P NMR spectra in the case of DIC indicated the formation of *E* and *Z* isomers of the respective phosphorylguanidine products (Figure FS114), whereas upon changing from DIC to the bulkier carbodiimide such as DCC and *N*-ethyl-*N*′-*tert*-butylcarbodiimide, we were able to obtain successfully only one isomer of phosphorylguanidine. Similar results were reported by Westerhausen et al.[20] in hydrophosphorylation catalyzed by alkali metals. We also extended our study in hydroacetylenation using phenylacetylene with three different carbodiimides such as DIC,

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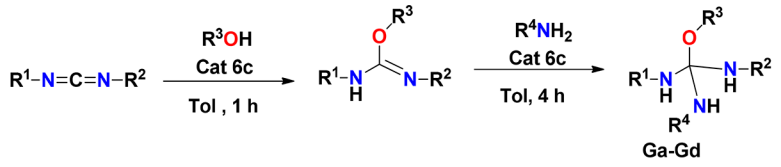
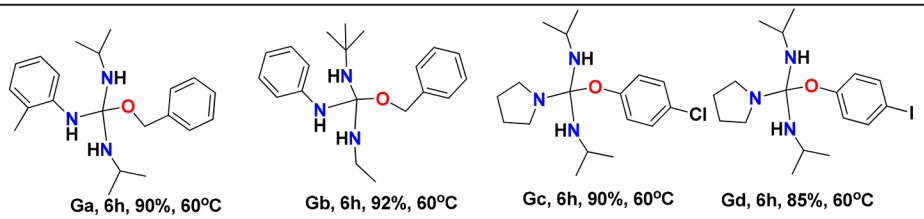
Table 5. Sequential Hydroalkoxylation−Hydroamination to Carbodiimides by Catalyst 6c[a]





[a]Reaction conditions: 4 mg of catalyst (0.005 mmol, ~0.5 mol %); cat./alcohol = 1/100; cat./carbodiimide = 1/100; 550 μL of $CDCl_3$; 60 °C. The yield was determined by ^1H NMR spectroscopy of the crude reaction mixture.

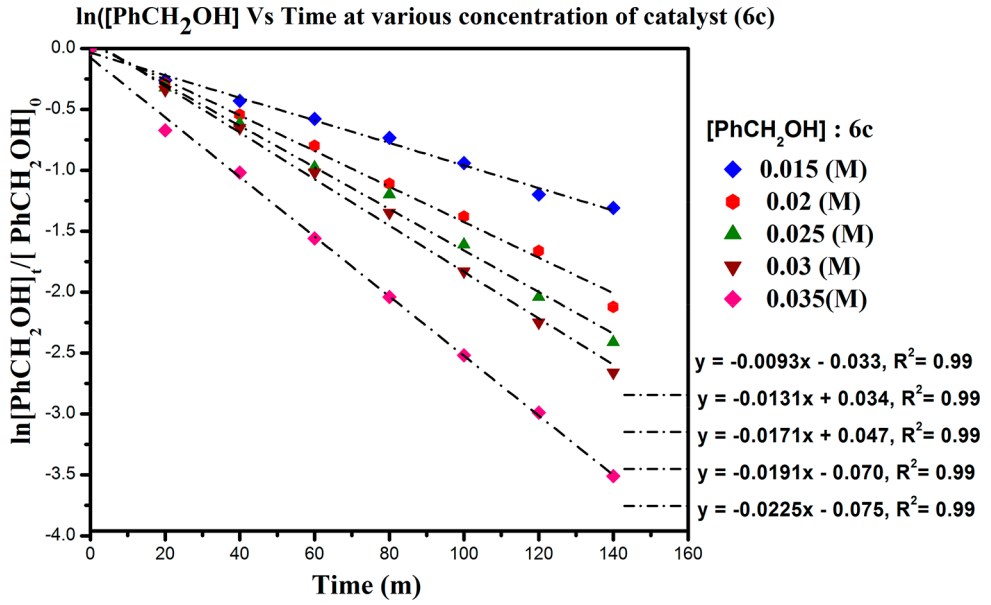


Figure 6. First-order kinetics plot for the reaction of benzyl alcohol with DIC catalyzed by **6c**.

DCC, and *N*-ethyl-*N*′-*tert*-butylcarbodiimide at 70 °C to give the corresponding products in high yield (**Da**−**Dc** in Table 3 and Figures FS121−FS124).

However, a dimerized product resulted when a propargylic substrate such as 3-(*N*,*N*-dimethylamino)-1-propyne or 5-methoxy-1-pentyne was used under identical conditions.[48] This observation showed the competition between alkyne oligomerization and insertion into heterocumulenes, revealing a lower energy barrier for insertion into the C−C bond, favoring the former process, rather than insertion into carbodiimides. However, when this reaction was performed with simple alkynes, such as 1-hexyne or 1-pentyne, it yielded the desired insertion product in excellent yield, providing substituted amidines (**Dd**−**Dg** in Table 3). Sterically bulky acetylene substrates such as ethynyltrimethylsilane required a longer reaction time (8 h) to achieve complete conversion (**Dh** and **Di** in Table 3). The scope of the catalytic addition of E−H bonds (E = N, O, S, P) was extended to isothiocyanates and isocyanates to illustrate the robust nature of catalyst **6c**. Using phenyl isothiocyanate and substituted phenyl isocyanate as the heterocumulene source, the insertion of amines, alcohols, thiols, and diphenylphosphine oxide was studied, and the results are presented in Table 4 (**Fa**−**Fi** in Table 4 and Figures FS125−FS135). The insertion of *N*,*N*-diisopropylamine, 2-methylaniline, and 2-fluoroaniline proceeded rapidly at room temperature to give the corresponding inserted products in quantitative yields (**Fa**−**Fc** in Table 4). In an analogous reaction, the addition of an aliphatic alcohol, 1-butanol, produced the corresponding product *O*-butyl phenylcarbamothioate (**Fd**). A cyclic product (**Fe**) was obtained within 1 h when 2-iodophenol was used as the source of alcohol. Aromatic thiols were smoothly inserted into the phenyl isothiocyanate to afford phenyl phenylcarbamodithioate (**Fh**) and 4-chlorophenyl phenylcarbamodithioate (**Fi**) in very good yields. However, the addition of diphenylphosphine oxide into phenyl isocyanate proved sluggish, and 95% conversion was obtained after 1 h of reaction time (**Fh** and **Fg** in Table 4). The enhanced reactivity of phenyl isothiocyanate and

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isocyanate with the various nucleophiles with respect to the carbodiimides was due to the stronger electrophilic character of the isothiocyanate C atom, as was already reported in previously published literature.[3−5]

Sequential Hydroelementation Reaction. We also wanted to explore the hydroamination and hydroalkoxylation reactions in a sequential manner using titanium catalyst **6c** (**Ga**−**Gd** in Table 5 and Figures FS136−FS145). The sequential hydroalkoxylation−hydroamination of carbodiimides was monitored by ^{1}H NMR spectra. In the initial step, benzyl alcohol was reacted with DIC in a 1:1 molar ratio in the presence of 5 mol % catalyst **6c**, followed by the addition of 1 equiv of arylamine, leading to the formation of the corresponding products (**Ga** and **Gb** in Table 5) in good yields. Because of the greater nucleophilic character of alcohol compared to amine, we presumed that the alcohol would initially react with DIC to afford an isourea derivative, which eventually reacted with the amine to produce 1-methoxy-*N*,*N*′,*N*″-trialkylmethanetriamine (**Ga** and **Gb** in Table 5), yielding up to 95% of the product within 6 h at 60 °C temperature. The ^{1}H NMR spectrum of **Ga** exhibits three separate broad resonances assigned to the NH peaks at δ_H 5.2−4.8 (Figure FS136). A similar NMR spectral observation was noted in the case of *N*-*tert*-butyl-*N*′-ethylcarbodiimide, which began as the heterocumulene source (**Gb** in Figure FS139).

Kinetic Study. To determine the initial rates of the hydroalkoxylation and hydroamination reactions, kinetic experiments were performed with respect to the starting material and catalyst **6c**. Reactions were performed with variable concentrations of catalyst **6c**, as well as DIC and benzyl alcohol while the other reagents' concentrations remained unchanged. Hence, in situ NMR spectroscopy experiments were carried out by loading complex **6c** (0.03, 0.04, 0.05, 0.06, and 0.07 M) from a stock solution and adding DIC (0.126 g, 1.0 mmol), $PhCH_2OH$ (0.108 g, 1.0 mmol), and $CDCl_3$ (1 mL) to it. The temperature of the solution mixture was set at 50 °C. At indicated time intervals, the solution was analyzed by ^{1}H NMR spectroscopy, which revealed that the rate law of the reactions displayed a first-order dependence on complex **6c** (Figures FS36−FS38). The reaction rate increased linearly with an increase in the amount of catalyst (Figure 6). The increase of the amount of DIC and $PhCH_2OH$ also led to linear acceleration of the reaction (Figures FS39−FS43). The rate of the reaction also displayed a first-order dependence on DIC (Figure FS43), $PhCH_2OH$ (Figure FS41), and complex **6c** (Figure FS38), giving rise to the following kinetic rate equation:

$$dp/dt = k_{obs}[DIC]^1[PhCH_2OH]^1[\mathbf{6c}]^1$$

We observed this in the case of the hydroamination reaction also. The rate of the reaction displayed first-order dependence on DIC (Figure FS53), $PhNH_2$ (Figure FS51), and complex **6c** (Figure FS49), giving rise to the following kinetic rate equation:

$$dp/dt = k_{obs}[DIC]^1[PhNH_2]^1[\mathbf{6c}]^1$$

The rate constants for the hydroamination and hydroalkoxylation reactions catalyzed by complex **6c** are given in Table TS12. This allows us to directly compare the k_{obs} values of each substrate and catalyst for two different reactions. The k_{obs} values for the hydroamination reaction are relatively higher than those for the hydroalkoxylation reaction with respect to each substrate and catalyst (k_{obs} = 0.023 M^{-1} m^{-1} for complex **6c** in hydroamination and 0.009 M^{-1} m^{-1} for complex **6c** in hydroalkoxylation; k_{obs} = 0.011 M^{-1} m^{-1} for aniline, 0.0031 M^{-1} m^{-1} for benzyl alcohol, and 0.009 M^{-1} m^{-1} for DIC in hydroamination and 0.0039 M^{-1} m^{-1} for DIC in hydroalkoxylation).

The activation parameters for the hydroalkoxylation and hydroamination reactions were determined from the Eyring and Arrhenius plots, with $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and E_a values of 11.22(4) kJ mol^{-1}, −243.43(7) J mol^{-1}, and 13.88 kJ mol^{-1} and 10.64(3) kJ mol^{-1}, −241.77(5) J mol^{-1}, and 12.89 kJ mol^{-1}, respectively (Figures 7 and FS44−FS46 and FS53−FS56),

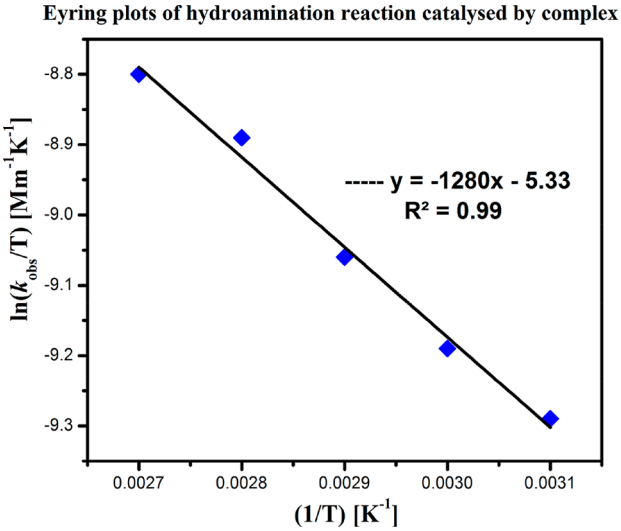

Figure 7. Eyring plots of $\ln(k_{obs}/T)$ (M m^{-1} K^{-1}) versus $1/T$ (K^{-1}) titanium (**6c**)-catalyzed reactions of $PhNH_2$ and DIC in $CDCl_3$ (0.4 ML) at various temperatures (1 equiv of aniline is present with respect to DIC). Reaction conditions: **6c** = 0.05 M, [DIC] = 1.0 M, and [$PhNH_2$] = 1.0 M in $CDCl_3$ (0.4 mL) having $\Delta H^{\ddagger}$ = 10.64(4) kJ mol^{-1} and $\Delta S^{\ddagger}$ = −241.77(3) J mol^{-1} K^{-1}.

displaying a higher activation barrier (E_a) for the hydroalkoxylation reaction over the hydroamination reaction. The large negative entropy values signify high-order transition states (TSs) at the rate-determining step.

The reaction of DIC with a series of substituted anilines revealed the effect of electronic substitution on the hydroamination reaction (Table TS22). Aniline substitution at both the meta (3-F) and para (4-Cl, 4-Br, 4-NO_2, 4-OMe, and NMe_2) positions with respect to DIC was studied under the standard protocol. It was observed that the rate of the hydroamination reaction was dependent on the electronic effect of the substituents of arylamines. The formation of the guanidine derivatives from these different substituted anilines was studied with respect to time (Table TS22, entries 1−7, and Figures FS57−FS63).

Continuous sampling was undertaken over the course of 0.5 h, and the conversions were determined by ^{1}H NMR spectroscopy analysis. Kinetic experiments showed a first-order rate equation with respect to substituted amine derivatives. A Hammett analysis was carried out (Figures FS64 and FS65) to establish the role of the electronic effects of the substituents on the reaction rate.[49] In a Hammett-type analysis, plots of the logarithmic values of the relative rate constants against a set of standard σ^- values (Hansch and

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colleagues) as well as against σ_p^+ (the Brown−Okamoto constant σ_p^+) were made[50] (Figures FS63 and FS64). A better correlation was found with the latter, having ρ values of 0.60 and 0.38 for σ_p^+ and σ^-, respectively. The positive slope values suggest $0 < \rho < 1$, the reaction is comparatively less sensitive to substituents than simple aniline, and a negative charge is built up at the reaction center. A positive slope with a ρ value of 0.60 was obtained (Figure 8), consistent with the formation of

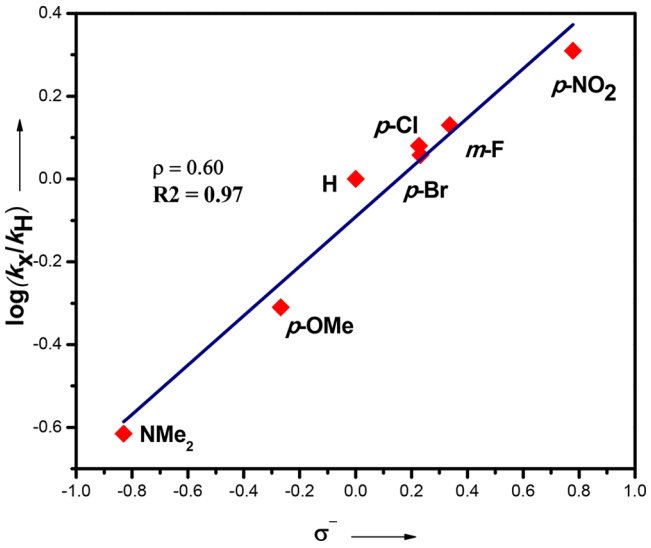


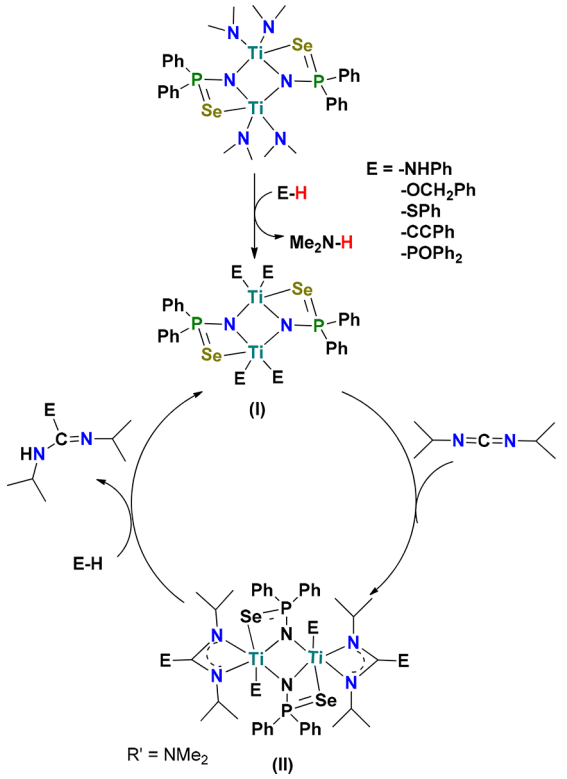
Figure 8. Hammett plot for the hydroamination reaction of DIC with various substituted amines on the basis of σ^-, ρ = 0.602.

negative charge/depletion of positive charge in the turnover-determining TS. A positive slope indicates that the rate of the reaction is consequently accelerated by the presence of an electron-withdrawing group, which helps to effectively stabilize the negatively charged TS.[51,52] Also, moving to the more delocalized 2-aminonaphthalene group, we observed a significant slowdown of the rate compared to any other systems (Figures FS146−FS148).

Most Plausible Mechanism. To explore the most plausible mechanism of the catalytic addition of E−H (E = O, N, C, S, P) to carbodiimides, we performed some controlled reactions. The stoichiometric reaction of catalyst **6c** with aniline, benzyl alcohol, and 2,4-di-*tert*-butylphenol independently showed that the complete displacement of the methyl peak of dimethylamidotitanium complexes occurred in each case by either anilide or alkoxide groups, respectively, at room temperature (Figures FS19−FS26).

However, the reaction of DIC with catalyst **6c** did not proceed at room temperature and needed 90 °C and 12 h to be completed (Figures FS27−FS29). The molecular structure of the titanium(IV) complex **7** formed by the complete displacement of the dimethylamino group of complex **6c** by DIC was isolated and confirmed by single-crystal X-ray diffraction analysis (Figure FS4). From these controlled experiments, we concluded that activation of the precatalyst is achieved by the addition of the nucleophile (E) moiety to generate the catalytically active species. On the basis of the above study, a plausible mechanism is presented in Scheme 4. The first step in this mechanism is the rapid protonolysis of catalyst **6c** by the E−H moiety, with displacement of the dimethylamine group, producing the active species (**I**). Migratory insertion of DIC to the corresponding Ti−E is in

Scheme 4. Plausible Mechanism of the Titanium-Mediated Catalytic Insertion of E−H Moieties into Carbodiimides



a rapid equilibrium (step 2), which produces complex **II**, that follows a protonolytic cleavage (step 3), with an additional molecule of the E−H species. This completes the catalytic cycle with the concomitant release of the target product and regeneration of the active species.

CONCLUSION

In summary, we have synthesized and characterized a series of mono- and dinuclear titanium(IV) complexes and established their solid-state structures. The dinuclear titanium(IV) complex **6c** acts as an efficient catalyst for the addition of E−H bonds (E = N, O, S, P, C) to heterocumulenes such as carbodiimides compared to the mononuclear analogues. More importantly, we have shown for the first time that the dinuclear titanium(IV) complex **6c** acts as a single competent catalyst for the chemoselective insertion of electron-rich alcohols, amines, phosphine oxide, and thiols with carbodiimides at ambient conditions with high degrees of conversion. The titanium catalyst **6c** displayed an unusual tolerance toward heteroatoms and functional groups, giving the corresponding insertion products in high yields and selectivity. The most plausible mechanisms of the catalytic addition of electron-rich E−H bonds (E = O, N, C, S, P) to carbodiimides are also described. Kinetic studies, together with Hammet analysis of the hydroamination reaction, indicate that protonolysis is the rate-determining step of the reaction.

EXPERIMENTAL SECTION

General Methods. All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or an argon-filled glovebox. Hydrocarbon solvents (*n*-pentane and toluene) were distilled under nitrogen from $LiAlH_4$ and stored in the glovebox. CH_2Cl_2 was dried over P_2O_5 and distilled

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under reflux conditions. Tetrahydrofuran was dried and deoxygenated by distillation over sodium benzophenone ketyl under argon and then distilled and dried over CaH_2 prior to being stored in the glovebox. ^1H (400 MHz), $^{13}C\{^1H\}$ (100 MHz), and $^{31}P\{^1H\}$ (100 MHz) NMR spectroscopy spectra were measured on a Bruker AVANCE III-400 spectrometer. Elemental analyses were performed on a Bruker EURO elemental analyzer at the Indian Institute of Technology Hyderabad. $[\{Ph_2P(X)NH\}_2C_6H_4]$ (**1a** and **1b**), $[trans\text{-}C_6H_{10}\{Ph_2P(X)NH\}_2]$ [X = S (**2a**) and Se (**2b**)] and $[HN(Ph_2PSe)_2]$ (**5b**) were prepared according to published procedures,[34−36] and $Ti(NMe_2)_4$ was purchased from Sigma-Aldrich India. NMR spectroscopy solvent C_6D_6 was purchased from Sigma-Aldrich India, dried over sodium/potassium, distilled, and stored in the glovebox.

*Preparation of $[\kappa^3\text{-}[C_6H_4\{NPh_2P(=Se)\}_2Ti(NMe_2)_2]]$ (**3b**).* In a 25 mL dry Schlenk flask, 100 mg (0.157 mmol) of ligand **1b** was placed, and 5 mL of dry toluene was added to it. To this solution was added dropwise at ambient temperature a mixture of $[Ti(NMe_2)_4]$ (35 mg, 0.157 mmol) and 5 mL of toluene. The resulting solution turned red immediately. The reaction mixture was kept under stirring conditions for another 6 h at ambient temperature. The solvent was thereafter evaporated in a vacuum to obtain a red solid, which was recrystallized from toluene into deep-red crystals at room temperature.

Yield: 120 mg (99%). ^1H NMR (400 MHz, C_6D_6): δ_H 8.01−7.95 (m, 8H, ArH), 7.11−6.93 (m, 10H, ArH), 6.64−6.54 (m, 6H, ArH), 2.97 (s, 12H, NMe_2). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C 136.7 (P−ArC), 135.9 (P−ArC), 132.2−132.0 (*o*-ArC), 130.8 (*o*-ArC), 127.8−127.6 (*m*- and *p*-ArC), 45.1 (N−CH_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ_P 59.7. Elem anal. Calcd for $C_{34}H_{36}N_4P_2Se_2Ti$ (768.4): C, 53.14; H, 4.72; N, 7.29. Found C, 52.73; H, 4.52; N, 7.01.

*Preparation of $[\kappa^3\text{-}[C_6H_4\{(NPh_2P=S)(N)\}Ti(NMe_2)]]_2]$ (**3c**).* In a 25 mL dry Schlenk flask, 100 mg (0.185 mmol) of ligand **1a** was placed, and 5 mL of dry toluene was added to it. To this solution was added dropwise a mixture of $[Ti(NMe_2)_4]$ (21 mg, 0.0925 mmol) and 5 mL of toluene. The resulting solution immediately turned red. The reaction mixture was kept under stirring conditions for another 12 h at ambient temperature. The solvent was thereafter evaporated in a vacuum to obtain a red solid, which was recrystallized from toluene into deep-red crystals at a temperature of −35 °C.

Yield: 146 mg (95%). ^1H NMR (400 MHz, C_6D_6): δ_H 7.99−7.94 (m, 8H, ArH), 7.14−7.11 (m, 2H, ArH), 6.99−6.96 (m, 16H, ArH), 6.62−6.61 (m, 2H, ArH), 2.97 (s, 12H, NMe_2). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C 137.7 (P−ArC), 132.3 (*o*-ArC), 132.2 (*o*-ArC), 129.2 (*m*-ArC), 128.4 (*m*-ArC), 125.6 (*p*-ArC), 44.6 (N−CH_3).$^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ_P 61.8. Elem anal. Calcd for $C_{54}H_{56}N_6P_2S_2Ti_2$ (1010.9): C, 64.16; H, 5.58; N, 8.31. Found: C, 63.82; H, 5.13; N, 8.04.

*Preparation of $[\kappa^3\text{-}[trans\text{-}C_6H_{10}\{NPh_2P(=S)\}_2Ti(NMe_2)_2]]$ (**4a**).*[36] In a 25 mL dry Schlenk flask, 100 mg (0.183 mmol) of ligand **2a** was placed, and 5 mL of dry toluene was added to it. To this solution was added a mixture of $[Ti(NMe_2)_4]$ (41 mg, 0.183 mmol) and 5 mL of toluene. The resulting reaction mixture immediately turned red. This solution was kept under stirring conditions for another 6 h at ambient temperature. The solvent was thereafter evaporated in vacuum to obtain a red-colored solid which was recrystallized from toluene into deep red crystals at a temperature of −35 °C.

Yield: 118 mg (95%). ^1H NMR (400 MHz, C_6D_6): δ_H = 8.00−7.73 (m, 8H, ArH), 7.38−7.24 (m, 12H, ArH), 3.24−3.22 (m, 2H, C*H*N), 3.01 (s, 12H, NMe_2), 1.76−1.75 (m, 2H, CH_2), 1.44−1.41 (m, 3H, CH_2), 1.39−1.32 (m, 2H, CH_2), 1.01−1.00 (m, 1H, CH_2) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C = 132.5 (P−ArC), 131.7 (*o*-ArC), 131.5 (*m*-ArC), 128.1 (*p*-ArC), 56.4.1 (C*H*N), 45.5 (N−CH_3), 35.5 (CH_2), 24.9 (CH_2) ppm; $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ_P = 66.7 ppm; Elemental Analysis: $C_{34}H_{42}N_4P_2S_2Ti$ (680.7): Calcd C 59.99, H 6.22, N 8.23. Found C 59.39, H 5.85, N 7.79.

*Preparation of $[\kappa^3\text{-}[trans\text{-}C_6H_{10}\{NPh_2P(=Se)\}_2Ti(NMe_2)_2]]$ (**4b**).* Complex **4b** was prepared using a procedure similar to that for the preparation of complex **4a** using 100 mg (0.157 mmol) of ligand **2b** and $[Ti(NMe_2)_4]$ (35 mg, 0.157 mmol).

Yield: 120 mg (99%). ^1H NMR (400 MHz, C_6D_6): δ_H 7.95−7.93 (m, 8H, ArH), 7.45−7.26 (m, 12H, ArH), 3.99 (s, 12H, $TiNMe_2$), 3.74−3.30 (m, 2H, C*H*N), 236−1.83 (m, 3H, CH_2), 1.52.1.49 (m, 5H, CH_2), 1.33−1.08 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C 132.4 (P−ArC), 132.3 (*o*-ArC), 130.8 (*m*-ArC), 129.2 (*p*-ArC), 47.5 (C*H*N), 44.7 (N−CH_3), 31.8 (CH_2), 25.4 (CH_2), 22.9 (CH_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ_P 73.4. Elem anal. Calcd for $C_{34}H_{42}N_4P_2Se_2Ti$ (774.5): C, 52.73; H, 5.47; N, 7.23. Found C, 52.21; H, 5.11; N, 6.98.

*Preparation of $[\{\kappa^2\text{-}N(PPh_2Se)_2\}_2Ti(NMe_2)_2]$ (**6b**).* In a 25 mL dry Schlenk flask, 100 mg (0.179 mmol) of the protic ligand $[\{Ph_2P(Se)\}_2NH]$ (**5b**) was placed, and 5 mL of dry toluene was added to it. To this solution was added a mixture of $[Ti(NMe_2)_4]$ (20.1 mg, 0.089 mmol) and 5 mL of toluene. The resulting solution immediately turned red. This solution was kept under stirring conditions for another 6 h at ambient temperature. The solvent was thereafter evaporated in a vacuum to obtain a red solid, which was recrystallized from toluene into deep-red crystals at a temperature of −35 °C.

Yield: 210 mg (98%). ^1H NMR (400 MHz, C_6D_6): δ_H 7.83−7.77 (m, 4H, ArH), 6.85−6.80 (m, 12H, ArH), 6.46−6.44 (m, 4H, ArH), 2.85 (s, 12H, NMe_2). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C 139.4 (P−ArC), 137.4 (P−ArC), 132.4 (*o*-ArC), 132.2 (*o*-ArC), 127.7 (*m*- and *p*-ArC), 121.6 (*p*-ArC), 120.8 (*p*-ArC), 46.9 (N−CH_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ_P 55.8. Elem anal. Calcd for $C_{59}H_{59}N_4P_4Se_4Ti$ (1311.7): C, 54.02; H, 4.53; N, 4.27. Found: C, 53.72; H, 4.19; N, 3.96.

*Preparation of $[\{\kappa^2\text{-}N(PPh_2Se)\}Ti(NMe_2)_2]_2$ (**6c**).* In a 25 mL dry Schlenk flask 100 mg (0.183 mmol) of ligand, **5b** was placed, and 5 mL of dry toluene was added to it. To this solution was added a mixture of $[Ti(NMe_2)_4]$ (21 mg, 0.0915 mmol) and 5 mL of toluene. The resulting solution immediately turned red. This solution was kept under stirring conditions for another 12 h at ambient temperature. The solvent was thereafter evaporated in a vacuum to obtain a red solid, which was recrystallized from toluene into deep-red crystals at a temperature of −35 °C.

Yield: 146 mg (96%). ^1H NMR (400 MHz, C_6D_6): δ_H 8.01−7.96 (m, 8H, ArH), 7.04−7.01 (m, 12H, ArH), 6.64−6.54 (m, 6H, ArH), 3.07 (s, 12H, NMe_2). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C 136.7 (P−ArC), 135.9 (P−ArC), 132.2 (*o*-ArC), 132.1 (*o*-ArC), 130.8 (*m*-ArC), 130.8 (*m*-ArC), 127.7 (*p*-ArC), 45.1 (N−CH_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ_P 59.7. Elem anal. Calcd for $C_{32}H_{44}N_6P_2Se_2Ti_2$ (828.3): C, 46.40; H, 5.35; N, 10.15. Found: C, 46.09; H, 4.99; N, 9.87.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01766.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and MS spectra and combustion analysis of all of the complexes and all of the insertion products **Aa**−**Ao**, **Ba**−**Bn**, **Ca**−**Ch**, **Da**−**Di**, **Ea**−**Ec**, **Fa**−**Fh**, and **Ga**−**Gd** and also full details of single-crystal X-ray diffraction analyses of the reported complexes **3b**, **3c**, **4b**, **6b**, and **6c** (PDF)

Accession Codes

CCDC 1846007−1846011 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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■ REFERENCES

(1) Zeng, X. Recent Advances in Catalytic Sequential Reactions Involving Hydroelement Addition to Carbon−Carbon Multiple Bonds. *Chem. Rev.* **2013**, *113*, 6864 and references cited therein. .

(2) (a) Ren, W.; Zi, G.; Fang, D. C.; Walter, M. D. A base-free thorium-terminal-imido metallocene: synthesis, structure, and reactivity. *Chem. - Eur. J.* **2011**, *17*, 12669−12682. (b) Stubbert, B. D.; Marks, T. J. Mechanistic Investigation of Intramolecular Aminoalkene and Aminoalkyne Hydroamination/Cyclization Catalyzed by Highly Electrophilic, Tetravalent Constrained Geometry 4d and 5f Complexes. Evidence for an M−N σ-Bonded Insertive Pathway. *J. Am. Chem. Soc.* **2007**, *129*, 6149−6167. (c) Stubbert, B. D.; Marks, T. J. Constrained Geometry Organoactinides as Versatile Catalysts for the Intramolecular Hydroamination/Cyclization of Primary and Secondary Amines Having Diverse Tethered C−C Unsaturation. *J. Am. Chem. Soc.* **2007**, *129*, 4253−4271. (d) Haskel, A.; Straub, T.; Eisen, M. S. Organoactinide-Catalyzed Intermolecular Hydroamination of Terminal Alkynes. *Organometallics* **1996**, *15*, 3773−3775. (e) Hayes, C. E.; Platel, R. H.; Schafer, L. L.; Leznoff, D. B. Diamido-Ether Actinide Complexes as Catalysts for the Intramolecular Hydroamination of Aminoalkenes. *Organometallics* **2012**, *31*, 6732−6740.

(3) (a) Weiss, C. J.; Wobser, S. D.; Marks, T. J. Organoactinide-Mediated Hydrothiolation of Terminal Alkynes with Aliphatic, Aromatic, and Benzylic Thiols. *J. Am. Chem. Soc.* **2009**, *131*, 2062−2063. (b) Weiss, C. J.; Wobser, S. D.; Marks, T. J. Lanthanide- and Actinide-Mediated Terminal Alkyne Hydrothiolation for the Catalytic Synthesis of Markovnikov Vinyl Sulfides. *Organometallics* **2010**, *29*, 6308−6320. (c) Weiss, C. J.; Marks, T. J. Perspective Organo-f-element catalysts for efficient and highly selective hydroalkoxylation and hydrothiolation. *Dalton Trans.* **2010**, *39*, 6576−6588.

(4) (a) Dash, A. K.; Wang, J. Q.; Eisen, M. S. Catalytic Hydrosilylation of Terminal Alkynes Promoted by Organoactinides. *Organometallics* **1999**, *18*, 4724−4741. (b) Dash, A. K.; Wang, J. X.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. Diverse catalytic activity of the cationic actinide complex $[(Et_2N)_3U][BPh_4]$ in the dimerization and hydrosilylation of terminal alkynes. Characterization of the first f-element alkyne π-complex $[(Et_2N)_2U(C{\equiv}C^tBu)(\eta^2\text{-}HC{\equiv}C^tBu)][BPh_4]$. *J. Organomet. Chem.* **2000**, *604*, 83−98.

(5) (a) Haskel, A.; Straub, T.; Dash, A. K.; Eisen, M. S. Oligomerization and Cross-Oligomerization of Terminal Alkynes Catalyzed by Organoactinide Complexes. *J. Am. Chem. Soc.* **1999**, *121*, 3014−3024. (b) Straub, T.; Haskel, A.; Eisen, M. S. Organoactinide-catalyzed oligomerization of terminal acetylenes. *J. Am. Chem. Soc.* **1995**, *117*, 6364−6365. (c) Wang, J. Q.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. Selective Dimerization of Terminal Alkynes Promoted by the Cationic Actinide Compound $[(Et_2N)_3U][BPh_4]$. Formation of the Alkyne π-Complex $[(Et_2N)_2U(C{\equiv}C^tBu)(\eta^2\text{-}HC{\equiv}C^tBu)][BPh_4]$. *Organometallics* **1999**, *18*, 2407−2409.

(6) Weetman, C.; Hill, M. S.; Mahon, M. F. Magnesium Catalysis for the Hydroboration of Carbodiimides. *Chem. - Eur. J.* **2016**, *22*, 7158−7162.

(7) Alonso, F.; Moglie, Y.; Radivoy, G.; Yus, M. Solvent- and catalyst-free regioselective hydrophosphanation of alkenes. *Green Chem.* **2012**, *14*, 2699−2702.

(8) (a) Ryu, J. S.; Marks, T. J.; McDonald, F. E. Organolanthanide-Catalyzed Intramolecular Hydroamination/Cyclization/Bicyclization of Sterically Encumbered Substrates. Scope, Selectivity, and Catalyst Thermal Stability for Amine-Tethered Unactivated 1,2-Disubstituted Alkenes. *J. Org. Chem.* **2004**, *69*, 1038−1052. (b) Seyam, A. M.; Stubbert, B. D.; Jensen, T. R.; O'Donnell, J. J.; Stern, C. L.; Marks, T. J. Organolanthanide constrained geometry complexes modified for catalysis: synthesis, structure, and aminoalkene hydroamination properties of a pyrrolidine-substituted constrained geometry organolutetium complex. *Inorg. Chim. Acta* **2004**, *357*, 4029−4035. (c) Ryken, S. A.; Schafer, L. L. N,O-Chelating Four-Membered Metallacyclic Titanium(IV) Complexes for Atom-Economic Catalytic Reactions. *Acc. Chem. Res.* **2015**, *48*, 2576−2586.

(9) (a) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. Chiral Neutral Zirconium Amidate Complexes for the Asymmetric Hydroamination of Alkenes. *Angew. Chem., Int. Ed.* **2007**, *46*, 354−358. (b) Takemiya, A.; Hartwig, J. F. Rhodium-Catalyzed Intramolecular, Anti-Markovnikov Hydroamination. Synthesis of 3-Arylpiperidine. *J. Am. Chem. Soc.* **2006**, *128*, 6042−6043. (c) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. A Highly Active Palladium Catalyst for Intermolecular Hydroamination. Factors that Control Reactivity and Additions of Functionalized Anilines to Dienes and Vinylarenes. *J. Am. Chem. Soc.* **2006**, *128*, 1828−1839. (d) Bender, C. F.; Widenhoefer, R. A. Platinum-Catalyzed Intramolecular Hydroamination of Unactivated Olefins with Secondary Alkylamines. *J. Am. Chem. Soc.* **2005**, *127*, 1070−1071. (e) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. Intermolecular Hydroamination of Terminal Alkynes Catalyzed by Organoactinide Complexes. Scope and Mechanistic Studies. *Organometallics* **2001**, *20*, 5017−5035. (f) Hayes, C. E.; Platel, R. H.; Schafer, L. L.; Leznoff, D. B. Diamido-Ether Actinide Complexes as Catalysts for the Intramolecular Hydroamination of Aminoalkenes. *Organometallics* **2012**, *31*, 6732−6740.

(10) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. 3,3′-Bis(trisarylsilyl)-Substituted Binaphtholate Rare Earth Metal Catalysts for Asymmetric Hydroamination. *J. Am. Chem. Soc.* **2006**, *128*, 3748−3759. (b) Riegert, D.; Collin, J.; Meddour, A.; Schulz, A.; Trifonov, A. Enantioselective Intramolecular Hydroamination Catalyzed by Lanthanide Ate Complexes Coordinated by N-Substituted (R)-1,1′-Binaphthyl-2,2′-diamido Ligands. *J. Org. Chem.* **2006**, *71*, 2514−2517. (c) Meyer, N.; Zulys, A.; Roesky, P. W. A Chiral-Bridged Aminotroponiminate Complex of Lutetium as Catalyst for the Asymmetric Hydroamination. *Organometallics* **2006**, *25*, 4179−4182. (d) Rastätter, M.; Zulys, A.; Roesky, P. W. Bis(phosphinimino)-methanide rare earth amides: synthesis, structure, and catalysis of hydroamination/cyclization, hydrosilylation, and sequential hydroamination/hydrosilylation. *Chem. - Eur. J.* **2007**, *13*, 3606−3616.

(11) (a) Crimmin, M. R.; Casely, I. J.; Hill, M. S. Calcium-Mediated Intramolecular Hydroamination Catalysis. *J. Am. Chem. Soc.* **2005**, *127*, 2042−2043. (b) Datta, S.; Roesky, P. W.; Blechert, S. Aminotroponate and Aminotroponiminate Calcium Amides as Catalysts for the Hydroamination/Cyclization Catalysis. *Organometallics* **2007**, *26*, 4392−4394. (c) Datta, S.; Gamer, M. T.; Roesky, P. W. Aminotroponiminate Complexes of the Heavy Alkaline Earth and the Divalent Lanthanide Metals as Catalysts for the Hydroamination/Cyclization Reaction. *Organometallics* **2008**, *27*, 1207−1213.

(12) Zhang, W. X.; Xu, L.; Xi, Z. Recent development of synthetic preparation methods for guanidines via transition metal catalysis. *Chem. Commun.* **2015**, *51*, 254−265.

DOI: 10.1021/acs.inorgchem.8b01766
Inorg. Chem. XXXX, XXX, XXX−XXX

(13) Zarate, S. G.; Santana, A. G.; Bastida, A.; Revuelta. Synthetic approaches to heterocyclic guanidines with biological activity: An update. J. *Curr. Org. Chem.* **2014**, *18*, 2711−2749.
(14) Ishikawa, T.; Kumamoto, T. Guanidines in Organic Synthesis. *Synthesis* **2006**, *2006*, 737−752.
(15) Batrice, R. J.; Eisen, M. S. Catalytic insertion of E−H bonds (E = C, N, P, S) into heterocumulenes by amido−actinide complexes. *Chem. Sci.* **2016**, *7*, 939−944.
(16) Liu, H.; Fridman, N.; Tamm, M.; Eisen, M. S. Addition of E−H (E = N, P, C, O, S) Bonds to Heterocumulenes Catalyzed by Benzimidazolin-2-iminato Actinide Complexes. *Organometallics* **2017**, *36*, 3896−3903.
(17) Karmel, I. S. R.; Tamm, M.; Eisen, M. S. Actinide-Mediated Catalytic Addition of E-H Bonds (E = N, P, S) to Carbodiimides, Isocyanates, and Isothiocyanates. *Angew. Chem.* **2015**, *127*, 12599−12602.
(18) Batrice, R. J.; Kefalidis, C. E.; Maron, L.; Eisen, M. S. Actinide-Catalyzed Intermolecular Addition of Alcohols to Carbodiimides. *J. Am. Chem. Soc.* **2016**, *138*, 2114−2117.
(19) Arrowsmith, M.; Crimmin, M. R.; Hill, M. S.; Lomas, S. L.; Heng, M. S.; Hitchcock, P. B.; Kociok-Kohn, G. Catalytic hydroacetylenation of carbodiimides with homoleptic alkaline earth hexamethyldisilazides. *Dalton Trans.* **2014**, *43*, 14249−14256.
(20) Harling, S. M.; Gorls, H.; Krieck, S.; Westerhausen, M. Potassium-Mediated Hydrophosphorylation of Heterocumulenes with Diarylphosphane Oxide and Sulfide. *Inorg. Chem.* **2016**, *55*, 10741−10750.
(21) Ghatak, T.; Fridman, N.; Eisen, M. S. Actinide Complexes Possessing Six-Membered N-Heterocyclic Iminato Moieties: Synthesis and Reactivity. *Organometallics* **2017**, *36*, 1296−1302.
(22) Schwamm, R. J.; Coles, M. P. Catalytic C−C Bond Formation Promoted by Organo- and Amidomagnesium(II) Compounds. *Organometallics* **2013**, *32*, 5277−5280.
(23) Bhattacharjee, J.; Sachdeva, M.; Banerjee, I.; Panda, T. K. Zinc-Catalyzed Guanylation Reaction of Amines to Carbodiimides/Isocyanate Leading to of Guanidines/Urea Derivatives Formation. *J. Chem. Sci.* **2016**, *128*, 875−881.
(24) (a) Tsurugi, H.; Ohnishi, R.; Kaneko, H.; Panda, T. K.; Mashima, K. Controlled Benzylation of α-Diimine Ligands Bound to Zirconium and Hafnium: An Alternative Method for Preparing Mono- and Bis(amido)M(CH_2Ph)n (n = 2, 3) Complexes as Catalyst Precursors for Isospecific Polymerization of α-Olefins. *Organometallics* **2009**, *28*, 680−687. (b) Panda, T. K.; Tsurugi, H.; Pal, K.; Kaneko, H.; Mashima, K. Highly Reactive Metal−Nitrogen Bond Induced C−H Bond Activation and Azametallacycle Formation. *Organometallics* **2010**, *29*, 34−37. (c) Naktode, K.; Kottalanka, R. K.; Panda, T. K. N-(2, 6-Dimethylphenyl) diphenylphosphinamine chalcogenides (S, Se) and a zirconium complex possessing phosphanylamide in the coordination sphere. *New J. Chem.* **2012**, *36*, 2280−2285.
(25) Schafer, L. L.; Yim, J. C. H.; Yonson, N. Transition-Metal-Catalyzed Hydroamination Reactions. *Metal-Catalyzed Cross-Coupling Reactions and More*; Wiley: New York, 2014; pp 1135−1258.
(26) (a) Chong, E.; Garcia, P.; Schafer, L. L. Hydroaminoalkylation: Early-Transition-Metal-Catalyzed α-Alkylation of Amines. *Synthesis* **2014**, *46*, 2884−2896. (b) Ryken, A. S.; Schafer, L. L. N,O-Chelating Four-Membered Metallacyclic Titanium(IV) Complexes for Atom-Economic Catalytic Reactions. *Acc. Chem. Res.* **2015**, *48*, 2576−2586.
(27) Stanford, M. J.; Dove, A. P. Stereocontrolled ring-opening polymerisation of Lactide. *Chem. Soc. Rev.* **2010**, *39*, 486−494.
(28) Galli, P.; Vecellio, G. Technology: driving force behind innovation and growth of polyolefins. *Prog. Polym. Sci.* **2001**, *26*, 1287−1336.
(29) Denmark, S. E.; Fu, J. Catalytic Enantioselective Addition of Allylic Organometallic Reagents to Aldehydes and Ketones. *Chem. Rev.* **2003**, *103*, 2763−2794.
(30) Schetter, B.; Ziemer, B.; Schnakenburg; Mahrwald, R. Tetranuclear BINOL−Titanium Complex in Selective Direct Aldol Additions. *J. Org. Chem.* **2008**, *73*, 813−819.
(31) Talsi, E. P.; Samsonenko, D. G.; Bryliakov, K. P. Titanium salan catalysts for the asymmetric epoxidation of alkenes: steric and electronic factors governing the activity and enantioselectivity. *Chem. - Eur. J.* **2014**, *20*, 14329−14335.
(32) (a) Mullins, S. M.; Duncan, A. P.; Bergman, R. G.; Arnold, J. Reactivity of a Titanium Dinitrogen Complex Supported by Guanidinate Ligands: Investigation of Solution Behavior and a Novel Rearrangement of Guanidinate. *Inorg. Chem.* **2001**, *40*, 6952−6963. (b) Johnson, J. S.; Bergman, R. G. Imidotitanium Complexes as Hydroamination Catalysts: Substantially Enhanced Reactivity from an Unexpected Cyclopentadienide/Amide Ligand Exchange. *J. Am. Chem. Soc.* **2001**, *123*, 2923−2924. (c) Kilgore, U. J.; Basuli, F.; Huffman, J. C.; Mindiola, D. J. Aryl Isocyanate, Carbodiimide, and Isocyanide Derived Prepared from Carbon Dioxide. A Metathetical Group-Transfer Tale Involving a Titanium-Imide Zwitterion. *Inorg. Chem.* **2006**, *45*, 487−489. (d) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. Intramolecular C-H Activation Reactions Derived From a Terminal Titanium Neopentylidene Functionality. Redox Controlled 1,2-Addition and α-Hydrogen Abstraction Reactions. *Organometallics* **2005**, *24*, 3321−3334. (e) Mindiola, D. J. Carboamination Reactions Using Titanium Pre-catalysts. A Catalytic Prospect to Preparing Conjugated C-N/C-C Frameworks. *Comments Inorg. Chem.* **2008**, *29*, 73−92.
(33) (a) Tonks, I. A.; Meier, J. C.; Bercaw, J. E. Titanium complexes supported by pyridine-bis(phenolate) ligands: active catalysts for intermolecular hydroamination or trimerization of alkynes. *Organometallics* **2013**, *32*, 3451. (b) Davis-Gilbert, Z. W.; Tonks, I. A. Titanium redox catalysis: insights and applications of an earth-abundant base metal. *Dalton Trans.* **2017**, *46*, 11522. (c) Cao, C.; Ciszewski, J. T.; Odom, A. L. Hydroamination of alkynes catalyzed by a titanium pyrrolyl complex. *Organometallics* **2001**, *20*, 5011−5013. (d) Li, Y.; Shi, Y.; Odom, A. L. Titanium Hydrazido Complexes: Synthesis, Structure, Reactivity, and Relevance to Alkyne Hydroamination. *J. Am. Chem. Soc.* **2004**, *126*, 1794−1803. (e) Li, Y.; Shi, Y.; Odom, A. L. Titanium Hydrazido Complexes: Synthesis, Structure, Reactivity, and Relevance to Alkyne Hydroamination. *J. Am. Chem. Soc.* **2004**, *126*, 1794−1803.
(34) (a) Perrier, A.; Comte, V.; Moïse, C.; Gendre, P. L. First Titanium-Catalyzed 1,4-Hydrophosphination of 1,3-Dienes. *Chem. - Eur. J.* **2010**, *16*, 64−67. (b) Dörfler, J.; Bytyqi, B.; Hüller, S.; Mann, N. M.; Brahms, C.; Schmidtmann, M.; Doye, S. An Aminopyridinato Titanium Catalyst for the Intramolecular Hydroaminoalkylation of Secondary Aminoalkenes. *Adv. Synth. Catal.* **2015**, *357*, 2265−2276. (c) Heutling, A.; Pohlki, F.; Bytschkov, I.; Doye, S. Hydroamination/Hydrosilylation Sequence Catalyzed by Titanium Complexes. *Angew. Chem.* **2005**, *117*, 3011−3013.
(35) Naktode, K.; Das, S.; Bhattacharjee, J.; Nayek, H. P.; Panda, T. K. complexImidazolin-2-iminato Ligand-Supported Titanium Complexes as Catalysts for the Synthesis of Urea Derivatives. *Inorg. Chem.* **2016**, *55*, 1142−1153.
(36) Bhattacharjee, J.; Das, S.; Kottalanka, R. K.; Panda, T. K. Hydroamination of carbodiimides, isocyanates, and isothiocyanates by a bis(phosphinoselenoic amide) supported titanium(IV). *Dalton Trans.* **2016**, *45*, 17824−17832.
(37) Bhattacharjee, J.; Harinath, A.; Nayek, H. P.; Sarkar, A.; Panda, T. K. Highly Active and Iso-Selective Catalysts for the Ring-Opening Polymerization of Cyclic Esters using Group 2 Metal Initiators. *Chem. - Eur. J.* **2017**, *23*, 9319−9331.
(38) Ly, T. Q.; Slawin, A. M. Z.; Woollins, J. D. Synthesis, coordination chemistry and crystallographic studies of somebis-(aminophosphines). *J. Chem. Soc., Dalton Trans.* **1997**, 1611−1616.
(39) Zhang, F.; Song, H.; Zi, G. Synthesis, structure, and catalytic activity of titanium complexes with new chiral 11,12-diamino-9,10-dihydro-9,10-ethanoanthracene-based ligands. *J. Organomet. Chem.* **2010**, *695*, 1993−1999.
(40) Bratko, I.; Gomez, M. Polymetallic complexes linked to a single-frame ligand: cooperative effects in catalysis. *Dalton Trans.* **2013**, *42*, 10664−10681.

DOI: 10.1021/acs.inorgchem.8b01766
Inorg. Chem. XXXX, XXX, XXX−XXX

(41) (a) van den Beuken, E. K.; Feringa, B. L. Bimetallic catalysis by late transition metal complexes. *Tetrahedron* **1998**, *54*, 12985−13011. (b) Gavrilova, A. L.; Bosnich, B. Principles of Mononucleating and Binucleating Ligand Design. *Chem. Rev.* **2004**, *104*, 349−383. (c) Shibasaki, M.; Matsunaga, S. Design and application of linked-BINOL chiral ligands in bifunctional asymmetric catalysis. *Chem. Soc. Rev.* **2006**, *35*, 269−279. (d) Delferro, M.; Marks, T. J. Multinuclear Olefin Polymerization Catalysts. *Chem. Rev.* **2011**, *111*, 2450−2485. (e) Park, J.; Hong, S. Cooperative bimetallic catalysis in asymmetric transformations. *Chem. Soc. Rev.* **2012**, *41*, 6931−6943.

(42) Vance, D. H.; Czarnik, A. W. Functional group convergency in a binuclear dephosphorylation reagent. *J. Am. Chem. Soc.* **1993**, *115*, 12165−12166.

(43) (a) Young, M. J.; Chin, J. Dinuclear copper (II) complex that hydrolyzes RNA. *J. Am. Chem. Soc.* **1995**, *117*, 10577−10578. (b) Cacciapaglia, R.; Casnati, A.; Mandolini, L.; Reinhoudt, D. N.; Salvio, R.; Sartori, A.; Ungaro, R. Catalysis of Diribonucleoside Monophosphate Cleavage by Water Soluble Copper(II) Complexes of Calix[4]arene Based Nitrogen Ligands. *J. Am. Chem. Soc.* **2006**, *128*, 12322−12330.

(44) (a) Chapman, W. H.; Breslow, R. Selective Hydrolysis of Phosphate Esters, Nitrophenyl Phosphates and UpU, by Dimeric Zinc Complexes Depends on the Spacer Length. *J. Am. Chem. Soc.* **1995**, *117*, 5462−5469. (b) Yashiro, M.; Ishikubo, A.; Komiyama, M. Infrared response of multiwalled boron nitride nanotubes. *Chem. Commun.* **1997**, *0*, 83−84.

(45) Haak, R. M.; Wezenberg, S. J.; Kleij, A. W. Cooperative multimetallic catalysis using metallosalens. *Chem. Commun.* **2010**, *46*, 2713−2723 and references cited therein. .

(46) (a) Champouret, J.; Fawcett, Y. D. M.; Nodes, W. J.; Singh, K.; Solan, G. A. Spacially Confined M2 Centers (M = Fe, Co, Ni, Zn) on a Sterically Bulky Binucleating Support: Synthesis, Structures and Ethylene Oligomerization Studies. *Inorg. Chem.* **2006**, *45*, 9890−9900. (b) Rodriguez, B. A.; Delferro, M.; Marks, T. J. Bimetallic Effects for Enhanced Polar Comonomer Enchainment Selectivity in Catalytic Ethylene Polymerization. *J. Am. Chem. Soc.* **2009**, *131*, 5902−5919. (c) Radlauer, M. R.; Day, M. W.; Agapie, T. Dinickel Bi-sphenoxyiminato Complexes for the Polymerization of Ethylene and α-Olefins. *Organometallics* **2012**, *31*, 2231−2243.

(47) (a) Li, H.; Stern, C. L.; Marks, T. J. Significant Proximity and Cocatalyst Effects in Binuclear Catalysis for Olefin Polymerization. *Macromolecules* **2005**, *38*, 9015−9027. (b) Guo, N.; Stern, C. L.; Marks, T. J. Bimetallic Effects in Homopolymerization of Styrene and Copolymerization of Ethylene and Styrenic Comonomers: Scope, Kinetics, and Mechanism. *J. Am. Chem. Soc.* **2008**, *130*, 2246−2261. (c) Salata, M. R.; Marks, T. J. Catalyst Nuclearity Effects in Olefin Polymerization. Enhanced Activity and Comonomer Enchainment in Ethylene + Olefin Copolymerizations Mediated by Bimetallic Group 4 Phenoxyiminato Catalysts. *Macromolecules* **2009**, *42*, 1920−1933.

(48) Yi, W.; Zhang, J.; Li, M.; Chen, Z.; Zhou, Z. Synthesis, Structures, and Reactivity of Yttrium Alkyl and Alkynyl Complexes with Mixed Tp^{Me2}/Cp Ligands. *Inorg. Chem.* **2011**, *50*, 11813−11824.

(49) Hansch, C.; Leo, A.; Taft, R. W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* **1991**, *91*, 165.

(50) Brown, H. C.; Okamoto, Y. Electrophilic Substituent Constants. *J. Am. Chem. Soc.* **1958**, *80*, 4979−4987.

(51) Hammett, L. P. The Effect of Structure upon the Recations of Organic Compounds Benzene Derivatives. *J. Am. Chem. Soc.* **1937**, *59*, 96−103.

(52) Moerdyk, J. P.; Blake, G. A.; Chase, D. T.; Bielawski, C. W. Elucidation of Carbene Ambiphilicity Leading to the Discovery of Reversible Ammonia Activation. *J. Am. Chem. Soc.* **2013**, *135*, 18798−18801.

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