C−C and C−N Coupling Reactions of an Imidotitanium Complex with Isocyanides

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Received July 3, 2000

Reaction of the imidotitanium complex [(κ^3-N$_2$Npy)Ti(=N*t*Bu)(py)] (**1**) [N$_2$Npy = (2-C$_5$H$_4$N)C(Me)(CH$_2$NSiMe$_3$)$_2$] with 2,6-xylylisocyanide led to double insertion of the isocyanide into the imidotitanium bond and yielded the four-membered titanacycle [(κ^3-N$_2$Npy)Ti{N(tBu)C(=N-2,6-Me$_2$C$_6$H$_3$)C(=N-2,6-C$_6$H$_3$Me$_2$)}] (**2**), which was characterized by X-ray crystallography. While unreactive toward bulky arylisocyanides, **2** reacted with a whole series of isocyanides R−NC [R = Et, *n*Bu, *i*Pr, Cy, *t*Bu, PhCH$_2$, *p*-Tol, (R)-CH(CH$_3$)Ph] to give the iminoketene complexes [(κ^3-N$_2$Npy)Ti{N(*t*Bu)C[N(2,6-Me$_2$C$_6$H$_3$)]C(=C=NR)N(2,6-Me$_2$C$_6$H$_3$)]-(R = Et, **3a**; *n*Bu, **3b**; *i*Pr, **3c**; Cy, **3d**; *t*Bu, **3e**; PhCH$_2$, **3f**; *p*-Tol, **3g**; (R)-CH(CH$_3$)Ph, **3h**). Single-crystal X-ray structure analyses of **3d**, **3f**, and **3g** were carried out, which established the coordination of an imidoylketeneimene fragment to the metal center. The reaction of **1** with alkyl isocyanides bearing H atoms α to the NC group leads to a sequential coupling of 3 molar equiv of the isocyanide with the imido complex, yielding metal-bonded diaminodihydropyrimidine derivatives [(κ^3-N$_2$Npy)Ti{N(*t*Bu)[$-\overline{\text{C}{=}\text{NCH(R)N(CH}_2\text{R)CHC}}\cdot\text{NCH}_2\text{R}$}] (R = H, **4a**; CH$_3$, **4b**; C$_3H_7$, **4c**; Ph, **4d**) and [(κ^3-N$_2$Npy)Ti{N(*t*Bu)[$-\overline{\text{C}{=}\text{NCRR}'\text{N(CHRR}'\text{)CHC}}-$] NCHRR′}] (R,R′ = C$_5H_{10}$, **5a**; CH$_3$,CH$_3$, **5b**; Ph,CH$_3$, **5c**). An X-ray diffraction study of **4a** unambiguously established the structure of this type of organometallic complex. These products are thought to be formed in a reaction sequence involving intermediates that are analogous to the stable complexes **2** and **3a**−**h**. The latter are then converted to the N-heterocycles via a diazahexatriene generated through a 1,5-sigmatropic H-shift and the subsequent cyclization to give the pyrimidine derivatives.

Introduction

From the early work on terminal imidotitanium complexes one was tempted to conclude that these compounds were either relatively unreactive if coordinatively saturated or, alternatively, highly reactive, low-coordinate species of a transient nature.[1−3] More recently, the use of an appropriate set of monodentate or multifunctional polydentate ligands has provided a series of imidotitanium complexes that combine sufficient stability with an adequate reactivity to allow the systematic development of the reaction chemistry of the Ti=NR fragment.[2,3]

A strategy in which the thermal stability of an imidotitanium complex is achieved by coordinative saturation which, however, allows the *reversible* generation of a reactive low-coordinate species involves the use of a formally dianionic diamidopyridine ligand system (**A**) developed previously by us.[4,5] We have shown that the coordination of this ligand to titanium leads to stable monomeric imido complexes such as **1**.[6] This compound possesses labile pyridine and pyridyl functionalities

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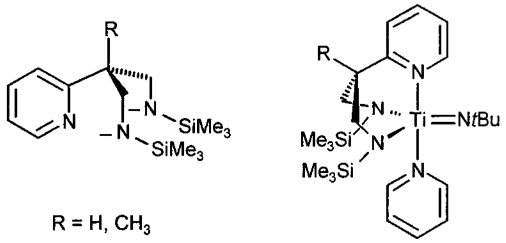
10.1021/om0005710 CCC: $19.00
Publication on Web 10/21/2000

Chart 1



A **1**

that, under appropriate reaction conditions, may dissociate to yield unsaturated and highly reactive species hitherto generally only accessible via *irreversible* thermolyses of appropriate precursors.[1a]

The high polarity of the imido−metal bond in the complexes of the titanium triad makes this structural unit the preferred point of attack for polar unsaturated organic substrates. Far from being an ancillary ligand, as in much of the chemistry of the imido complexes of the metals further to the right in the transition series,[7] the imidotitanium unit may be a synthon in element−nitrogen coupling reactions in organic synthesis. In this paper we describe the C−N and C−C− coupling reactions of the imidotitanium complex **1** with isocyanides, along with a mechanistic study of these transformations. They demonstrate that the patterns of reactivity that are observed may be useful in the synthesis of N-heterocycles. Three reports of the reaction of imido complexes with isocyanides have been published previously.[8] A part of this work has been communicated.[6]

Results and Discussion

Synthesis and Structural Characterization of [(κ^3-N$_2$Npy)Ti{N(tBu)C(=N-2,6-Me$_2$C$_6$H$_3$)C(=N-2,6-Me$_2$C$_6$H$_3$)}] (2). The reaction of the previously reported imido titanium compound [(κ^3-N$_2$Npy)Ti(=NtBu)(py)] (**1**)[6] with 2,6-xylylisocyanide was carried out with the aim of obtaining the product of a C−N coupling reaction, a metal-bonded carbodiimide. Such a reaction has been reported by Bergman and co-workers in their study of the reactivity of imido−zirconium and −iridium complexes toward *t*BuNC.[8a,b] The latter proved to be unreactive toward **1**, while a whole range of isocyanides studied in this work reacted immediately. However, no product of single C−N coupling reaction could be isolated with any of the substrates. The most straightforward reaction was that of **1** with xylylisocyanide, which cleanly gave the product of a double insertion into the imidotitanium bond, [(κ^3-N$_2$Npy)Ti{N(tBu)C(=N-2,6-Me$_2$C$_6$H$_3$)C(=N-2,6-Me$_2$C$_6$H$_3$)}] (**2**) (Scheme 1).

This complex is obtained as a dark green solid that is sparingly soluble in aromatic hydrocarbons but could be recrystallized from thf to yield crystals suitable for an X-ray diffraction study. Its molecular structure is depicted in Figure 1, and the principal bond lengths and angles are listed in Table 1.

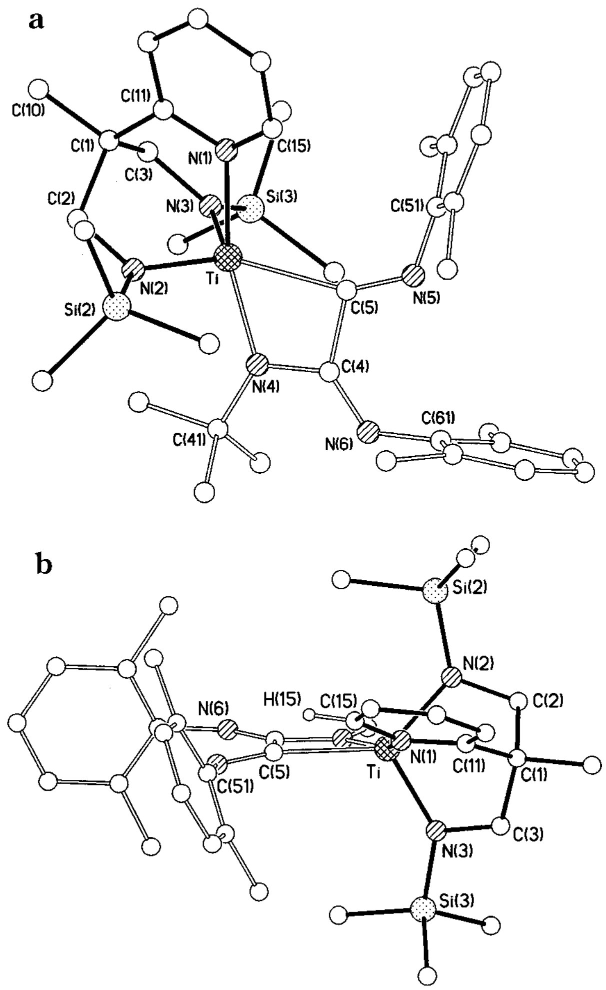
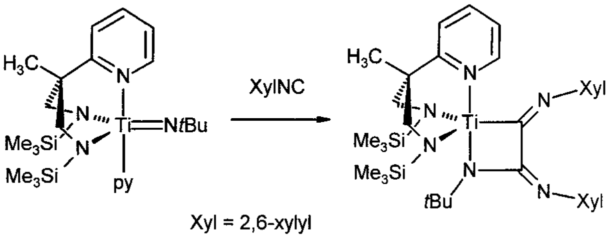


Figure 1. Molecular structure of complex **2**. The principal bond lengths and interbond angles are listed in Table 1.

Scheme 1. Double Insertion of 2,6-Xylylisocyanide into the Ti=NR Unit of 1 to Give the Titanacycle 2



1 **2**

Compound **2** has an interesting molecular geometry due to the coordination of the tridentate diamidopyridine ligand and the organometallic NCC fragment which is part of a metallacycle. It may be viewed as a highly distorted trigonal bipyramidal arrangement with the pyridyl-N atom and the *t*BuN unit derived from the imido ligand occupying the apical positions while the amido functions and C(5) of the metallacycle are in the equatorial plane. This results in an arrangement that is closely related to the postulated transition state structure in Ugi's turnstile mechanism for the polytopal rearrangement of pentacoordinate phosphorus compounds.[9]

There are two main deviations from ideal trigonal bipyramidal geometry. First the deviation from the ideal value of 180° by the angle between the "apical" atoms,

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Table 1. Selected Bond Lengths and Angles for Complexes 2, 3d, 3f, 3g, and 4a

	2	**3d**	**3f**	**3g**	**4a**
		(a) Lengths (Å)			
Ti−N(1)	2.195(9)	2.294(3)	2.346(5)	2.287(6)	2.282(2)
Ti−N(2)	1.899(9)	1.908(3)	1.906(4)	1.901(5)	1.937(2)
Ti−N(3)	1.900(8)	1.896(3)	1.900(4)	1.885(5)	1.890(2)
Ti−N(4)	2.024(8)	2.050(3)	2.058(4)	2.049(5)	2.035(2)
Ti−N(5)		2.012(3)	1.983(4)	2.013(5)	1.964(2
Ti−C(5)	2.249(11)				
N(4)−C(4)	1.36(1)	1.380(5)	1.372(7)	1.371(8)	1.379(3)
N(5)−C(5)	1.26(1)	1.422(5)	1.426(7)	1.415(8)	1.393(4)
C(4)−C(5)	1.57(1)	1.481(5)	1.480(7)	1.480(9)	1.485(4)
C(4)−N(6)	1.27(1)	1.295(5)	1.302(7)	1.294(8)	1.298(4)
C(5)−C(6)		1.325(5)	1.316(8)	1.331(9)	1.350(4)
N(2)−C(2)	1.45(1)	1.481(5)	1.464(7)	1.486(7)	1.474(3)
N(3)−C(3)	1.48(1)	1.483(5)	1.472(7)	1.478(7)	1.476(3)
C(6)−N(7)		1.226(5)	1.222(7)	1.224(8)	1.414(4)
N(5)−C(51)	1.397(9)	1.442(5)	1.447(5)	1.451(6)	1.462(4)
N(6)−C(7)					1.457(4)
N(6)−C(61)	1.40(1)	1.407(5)	1.397(5)	1.413(6)	
N(7)−C(71)		1.490(5)	1.471(7)	1.424(8)	
N(7)−C(7)					1.450(5)
		(b) Angles (deg)			
N(1)−Ti−N(2)	82.2(4)	77.8(1)	80.1(2)	78.1(2)	79.48(9)
N(1)−Ti−N(3)	90.1(4)	89.6(1)	86.0(2)	89.4(2)	85.64(9)
N(1)−Ti−N(4)	158.6(4)	166.6(1)	172.0(2)	167.8(2)	163.96(9)
N(1)−Ti−N(5)/C(5)	97.1(4)	90.6(1)	93.6(2)	91.5(2)	88.81(9)
N(2)−Ti−N(3)	107.7(4)	106.2(1)	108.5(2)	107.8(2)	108.5(1)
N(2)−Ti−N(4)	102.8(4)	101.4(1)	99.9(2)	101.0(2)	98.64(9)
N(2)−Ti−N(5)/C(5)	133.6(4)	137.0(1)	131.0(2)	135.3(2)	131.9(1)
N(3)−Ti−N(4)	107.7(4)	103.3(1)	101.5(2)	102.3(2)	109.9(1)
N(3)−Ti−N(5)/C(5)	118.7(4)	115.1(1)	119.6(2)	115.6(2)	117.0(1)
N(4)−Ti−N(5)/C(5)	64.2(4)	80.9(1)	80.3(2)	80.6(2)	80.60(9)
Ti−N(2)−C(2)	110.7(6)	112.4(2)	113.7(3)	112.1(4)	111.3(2)
Ti−N(3)−C(3)	112.2(7)	115.4(2)	113.9(3)	113.9(4)	115.7(2)
Ti−N(4)−C(4)	104.9(6)	116.7(3)	117.0(4)	116.6(4)	112.2(2)
Ti−N(5)−C(5)		113.2(3)	115.2(3)	113.6(4)	114.5(2)
Ti−C(5)−C(4)	88.7(6)				
Ti−N(5)−C(51)		134.3(3)	132.0(3)	134.2(4)	128.3(2)
Ti−C(5)−N(5)	153.0(8)				
N(2)−C(2)−C(1)	114.9(9)	115.9(3)	117.1(4)	116.4(5)	117.5(2)
N(3)−C(3)−C(1)	118.3(1)	117.1(3)	117.8(4)	119.3(6)	116.5(2)
N(4)−C(4)−N(6)	126.3(9)	123.4(4)	124.7(5)	123.4(6)	125.9(3)
N(5)−C(5)−C(4)	117.6(9)	116.5(3)	115.5(5)	116.0(6)	114.3(2)
N(5)−C(5)−C(6)		120.9(4)	120.8(5)	121.0(6)	127.5(3)
C(4)−C(5)−C(6)		122.1(4)	123.5(5)	122.7(7)	117.6(3)
C(5)−C(6)−N(7)		170.3(4)	170.8(6)	168.9(7)	120.7(3)
N(6)−C(6)−N(7)					116.8((3)
C(4)−N(6)−C(61)	126.5(9)	124.2(4)	125.2(5)	124.5(6)	
C(4)−N(6)−C(7)					112.6(6)
C(6)−N(7)−C(71)		121.0(4)	120.7(5)	124.1(6)	112.1(3)

N(1)−Ti−N(4) 158.6(4)°, is dictated by the steric strain of the azatitanacyclobutane ring, which enforces a N(4)−Ti−C(5) angle of 64.2(4)°. Second, the coordination at titanium deviates markedly from the anticipated C_s symmetry, with the "equatorial" angles N(2)−Ti−C(5) and N(3)−Ti−C(5) having values of 133.6(4)° and 118.7(4)°, respectively. The steric reasons for this large angular distortion can be seen by reference to Figure 1b, which shows a view of the molecule perpendicular to the N(2)−Ti−N(3) plane; an ortho hydrogen atom of the pyridyl ring is very close to the xylyl group, H(15)···C(51) 2.47 Å (sum of van der Waals radii 2.95 Å). It appears that the repulsion between these atoms not only causes the enlargement of N(2)−Ti−C(5) angle but forces the pyridyl ring from a vertical orientation by 12.6°.

The NMR spectroscopic data of **2** are very similar to those obtained for other complexes containing the diamidopyridine ligand. However, the signal of the H^6-proton in the pyridyl ring is observed at 7.41 ppm and thus at remarkably high field. The corresponding resonance in all other previously characterized compounds has been observed between δ 8.4 and 9.5 (the corresponding signal for the free amine is observed at 8.45 ppm).[4−6] This high-field shift is thought to be due to the location of the proton within the anisotropy cone of one of the xylyl groups. This interpretation is consistent with the very close contacts between the H^6 proton of the pyridyl [H(15)] and the xylyl group discussed above.

To our knowledge, compound **2** represents only the second example of a structurally characterized azatitanacyclobutane. We recently reported the reaction product of methylallene with the imidototanium complex **1** giving the metallacycle **I**, depicted in Figure 2.[10] The

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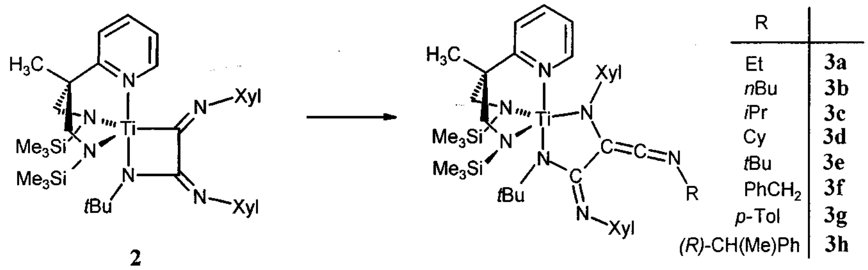
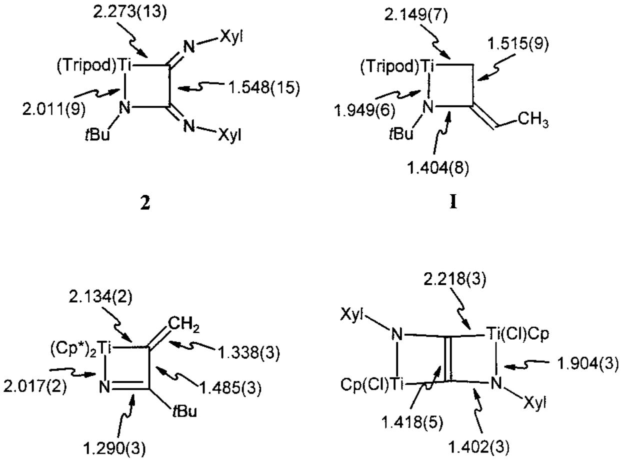
Scheme 2. Reaction of 2 with Isocyanides to Give the Imidoylketeneimine Complexes 3a−h



2

R	
Et	**3a**
*n*Bu	**3b**
*i*Pr	**3c**
Cy	**3d**
*t*Bu	**3e**
PhCH₂	**3f**
p-Tol	**3g**
(*R*)-CH(Me)Ph	**3h**



2 I

II III

Figure 2. Comparison of the metric parameters of the four-membered metallacycle in **2** with the titanacycles in **I**−**III** reported in the literature; tripod = ligand **A**.

only other structures reported in the literature that are related to this system are the azatinanacyclobutenes $[Cp^*_2Ti\{\kappa\text{-}C,N\text{-}N{=}(t\text{Bu})\text{-}C({=}CH_2)\}]$ (**II**) and $[(CpTiCl)_2\text{-}(\mu\text{-}N_2C_2Xyl_2)]$ (**III**).[11,12]

It is instructive to compare the bond lengths in the metallacycles of **2** and **I**−**III**. The Ti−N distances vary between 1.904(3) Å in **I** and 2.024(8) Å in **2** and do not seem to be strongly affected by the substituent (or absence of a substituent) at the nitrogen atom. The Ti−C distance of 2.249(11) Å in **2** is the greatest in all the structures compared in Figure 2, which may be a consequence of interligand repulsion between the xylyl group and the pyridyl unit of the tripodal ancillary ligand.

Synthesis and Structural Characterization of the Iminoketene Complexes $[(\kappa^3\text{-}N_2Npy)Ti\{N\text{-}(t\text{Bu})C[N(2,6\text{-}Me_2C_6H_3)]C({=}C{=}NR)N(2,6\text{-}Me_2C_6H_3)\}]$ (R = Et, 3a; *n*Bu, 3b; *i*Pr, 3c; Cy, 3d; *t*Bu, 3e; PhCH₂, 3f; *p*-Tol, 3g; (R)-CH(CH₃)Ph, 3h). The clean reaction of **1** with xylylisocyanide to give complex **2** is probably a consequence of the steric demand of the 2,6-xylyl groups, which suppresses further reaction with excess xylylisocyanide. Another factor may be the low solubility of the reaction product in benzene, which leads to immediate precipitation upon its formation. That the metallacycle **2** is by no means an unreactive species is apparent from its interaction with isocyanides other than the bulky 2,6-xylylisocyanide or 2,6-diisopropylphenylisocyanide.

Table 2. Characteristic Spectroscopic Data of the Imidoyl Iminoketene Complexes

compound	IR ν(iminoketene), cm^{-1}	^{13}C NMR $C_\beta{=}C_\alpha{=}N$, ppm
3a	1976	102.3, 193.1
3b	1969	101.7, 193.6
3c	1973	102.8, 190.3
3d	1967	104.0, 187.1
3e	1967	102.6, 197.2
3f	1982	103.4, 189.7
3g	1954	105.0, 200.4
3h	1963	104.8, 193.6

Reaction of **2** with a whole series of isocyanides R−NC [R = Et, *n*Bu, *i*Pr, Cy, *t*Bu, PhCH₂, *p*-Tol, (R)-CH(CH₃)-Ph] led to the selective conversion to the complexes **3a**−**h**, which contain an imidoylketimine unit coordinated to the metal center and are the products of a triple isocyanide coupling reaction (Scheme 2).

Whereas compounds **3a**, **3b**, **3f**, and **3g** are generated instantaneously at ambient temperature, the complete conversion to **3c**, **3d**, and **3h** takes ca. 30 min, and the reaction with *t*BuNC requires 24 h for completion. The most characteristic spectroscopic featutes of **3a**−**h** are the infrared band of the keteneimine unit that is observed between 1964 and 1982 cm^{-1} and the ^{13}C NMR chemical shifts of the same fragment, which are given in Table 2. The imine band that would be expected in the range between 1540 and 1615 cm^{-1} is obscured by the absorptions of the pyridyl unit. The proximity of one of the xylyl rings and the pyridyl ring again leads to a significant high-field shift of the resonance attributable to the H^6 proton of the pyridyl unit, which is observed below 7.15 ppm in all cases.

The unusual combination of polar unsaturated functional groups in the organometallic fragment obtained by imido−isocyanide coupling made it desirable to obtain detailed structural data for this type of complex. Single crystals of compounds **3a**, **3d**, **3f**, and **3g** were obtained, and single-crystal X-ray structure analyses of all four complexes were carried out. Although the basic features of its molecular structure are established, due to the poor quality of the data obtained for **3a**, a discussion of the structural parameters of this compound is not given. The molecular structures of **3d**, **3f**, and **3g** are shown in Figure 3, and the principal bond lengths and angles are listed in Table 1.

The five-membered azatitanacyclopentane ring, with the iminoketene [C(5)−C(6)−N(7)] and an imine [C(4)−N(6)] group adjacent to each other, is the structural centerpiece in the molecular structures of the three complexes. The keteneimine unit is positioned between the two 2,6-xylyl groups, which, most probably for steric reasons, are oriented orthogonal to it. The reduced steric strain imposed by the five-membered metallacycle in

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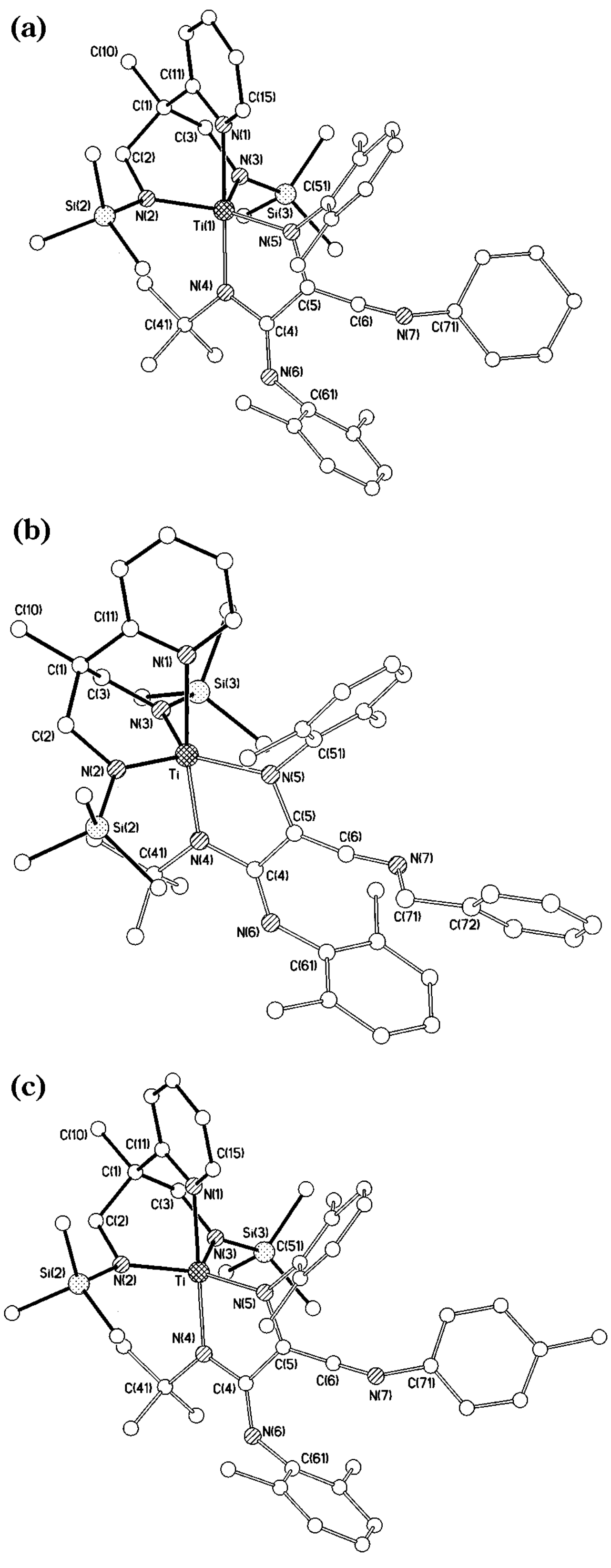

Figure 3. Molecular structure of complexes **3d** (a), **3f** (b), and **3g** (c). The principal bond lengths and interbond angles of all three compounds are listed in Table 1.

comparison with the four-membered ring in **2** is reflected in the reduced distortion of the molecular geometry from an idealized trigonal bipyramidal arrangement. There is still a significant deviation of the angle N(3)−Ti−N(4) from 180° [**3d**, 166.6(1)°; **3f**, 172.0(2)°; **3g**, 167.8(2)°] but considerably less so than in **2** [158.6(4)°]. The three molecular structures show distortions from idealized C_s symmetry very similar to those illustrated in Figure 1b for compound **2**, with the equatorial angles N(2)−Ti−N(5) in **3d**, **3f**, and **3g** [range 131.0(2)−137(1)°] being very much larger than the equivalent equatorial angles N(3)−Ti−N(5) [range 115.1(1)−119.6(2)°] and the pyridyl ring being tilted from vertical relative to the T−N(2)−N(3) plane (dihedral angles **3d**, 77.4°; **3f**, 86.3°; **3g**, 77.1°). These distortions are again attributable to repulsion between the pyridyl hydrogen atom H(15) and the xylyl unit, which are in very close contact [H(15)···C(51) **3d**, 2.37; **3f**, 2.38; **3g**, 2.36 Å]. This proton, H^6 in the NMR spectrum, is therefore expected to lie in the magnetic anisotropy cone of the aryl ring, which is consistent with the observation of the ^1H NMR resonance at high field as discussed above. The amido-N−Ti bond lengths as well as the pyridyl-N−Ti bond lengths are unexceptional.

Compounds **3d**, **3f**, and **3g** are the first structurally characterized complexes in which a iminoketene group and an imino group have a mutual *Z*-configuration. Both fragments are not located in the same plane due to steric interactions between the iminoketene unit and the neigboring xylyl groups. The torsion angles N(6)−C(4)−C(5)−N(5) and C(6)−C(5)−N(5)−C(51) are 21.0° and −19.5° (**3d**), 7.8° and −7.8° (**3f**), and 13.8° and −13.8° (**3g**).

There are two examplexs of complexes in the literature in which an imino group and an iminoketene unit adopt an *E*-configuration. Gerlach and Arnold reported the crystal structure analysis of $[(Me_3Si)_2N\}_2V\{tBuN{=}C(Me)C(C{=}C{=}NtBu)NtBu\}]$ [C−C 1.345(4), C−N 1.205(4) Å, C−C−N 171.7(3)°],[13] and Rothwell et al. synthesized $[Ta(OC_6H_3iPr_2\text{-}2,6)_2Cl_2\{tBuN{=}CHC(C{=}CNtBu)NtBu)\}]$ [C−C 1.338(6), C−N 1.206(5) Å, C−C−N 169.3(4)°].[14] The structural parameters of the iminoketene units found in **3d**, **3f**, and **3g** are thus very similar: C−C 1.316(8)−1.331(9) Å, C−N 1.224(8)−1.226(5) Å, C−C−N 168.9(7)−170.8(6)° (Table 1).

Reaction of the Imidotitanium Complex 2 with Isocyanides Bearing Two or Three α-Hydrogen Atoms. The reaction of methyl isocyanide with **1** occurred spontaneously and highly selectively at ambient temperature. The conversion to a single product **4a** was complete after addition of 3 molar equiv of the isocyanide, as was monitored by NMR spectroscopy. Even if small quantities of the substrate were titrated to the solution of the imido complex, at 200 K in toluene-d_8, no intermediates could be detected in the ^1H NMR spectra, which were recorded during the procedure. The ^1H and ^{13}C NMR spectra of the reaction product were consistent with the formation of a metal-bound diaminodihydropyrimidine, as shown in Scheme 3.

The molecular structure of the reaction product **4a** was established by a single-crystal X-ray structure analysis and is displayed in Figure 4, while the principal bond lengths and interbond angles are listed in Table 1.

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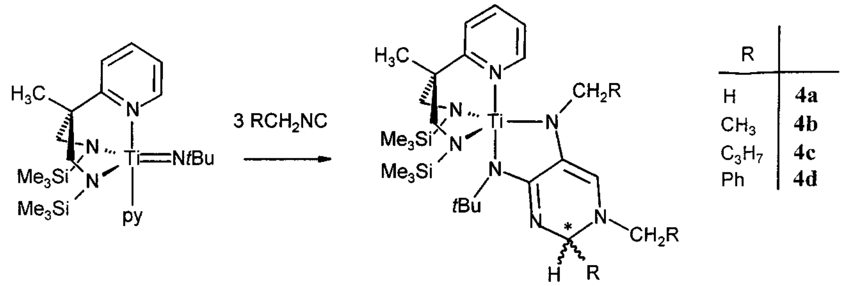
[13] Gerlach, C. P.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 4795.

[14] Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 3232.

Scheme 3. Reaction of 1 with Alkylisocyanides to Give 4a−d Containing a Metal-Bound Diaminidihydropyrimidine Ligand



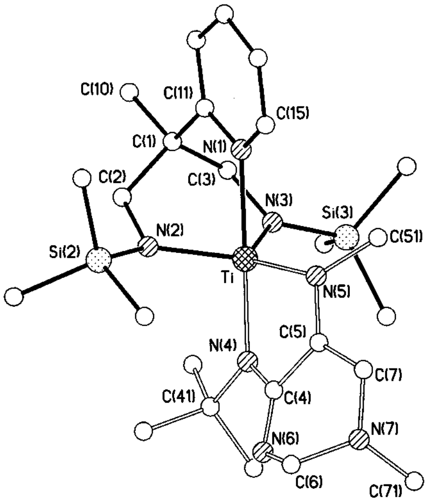


Figure 4. Molecular structure of complex **4a**. The principal bond lengths and interbond angles are listed in Table 1.

As in the molecular structures discussed in the previous section, complex **4a** contains a central five-coordinate Ti atom with a distorted trigonal-bipyramidal arrangement of the N-donor atoms [N(1)−Ti−N(41) 163.94(9)°]. The apical positions are occupied by the pyridyl [Ti−N(41) 2.282(2) Å] and the *tert*-butyl amide fragment N-donor atoms. The Ti═N*t*Bu unit of **1** has undergone C−N and C−C coupling (with concomitant C−H bond migration) with three molecules of MeNC to form a coordinated 3-methyl-5,6-diamino-2,3-dihydropyrimidine derivative. In the ^{1}H NMR sprectrum of **4a** the signal of the methylene protons in the heterocycle is observed at δ 4.86, while that of the CH group appears at 5.45 ppm.

To establish the generality of this reaction, the analogous conversion was carried out using EtNC, *n*-BuNC, and PhCH$_2$NC, which yielded the cyclization products $[(\kappa^3\text{-N}_2\text{Npy})\text{Ti}\{\eta^2\text{-NCH}_2\text{R}\}[-\overline{\text{C}{=}\text{NCH(R)N(CH}_2\text{R)CHC}}\text{-N}t\text{Bu}]$ (R = CH$_3$, **4b**; C$_3$H$_7$, **4c**; Ph, **4d**) (Scheme 3). Their formulation was established by elemental analysis and NMR spectroscopy. While the resonance patterns in the ^{1}H and ^{13}C NMR spectra are entirely analogous to those of **4a**, the presence of a chiral center in the ring structure of the coupling product renders the trimethylsilyl groups and the methylene groups of the ligand diastereotopic and thus chemically inequivalent.

Reaction of the Imidotitanium Complex 2 with Isocyanides Bearing One α-Hydrogen Atom. The cascade of C−N and C−C coupling reactions yielding the heterocyclic derivatives of **4** described above leads to the formation of stereogenic centers located on tertiary carbon atoms. To assess whether it was possible to obtain quaternary carbon centers in this position, the reaction of the imido complex **1** was carried out using the secondary alkyl isocyanides CyNC, *i*PrNC, and *(R)*-Ph(Me)CHNC. In all three cases an immediate conversion to the titanium complexes bearing the N-heterocycles $[(\kappa^3\text{-N}_2\text{Npy})\text{Ti}\{\text{N}t\text{Bu}\}\{\eta^2\text{-NCHRR}'\}[-\overline{\text{C}{=}\text{NCRR}'\text{N(CHRR}'\text{)CHC}}\text{-}]]$ (R,R′ = C$_5$H$_{10}$, **5a**; CH$_3$, CH$_3$, **5b**; Ph,CH$_3$, **5c**) was observed (Scheme 4).

Whereas compounds **5a** and **5c** are achiral, a mixture of two diastereomers in a relative ratio of 4:1 is obtained for **5b**. This is clearly a consequence of the de novo generation of the stereogenic center in the ring, which is thought to occur through an intermediate containing an sp^2-carbon in this position (vide infra). The formation of both diastereomers in nonequal amounts is due to the presence of two additional *R*-configurated chiral centers in the molecule which do not undergo a transformation and provide the chiral environment that favors one of the two diastereomers formed in the reaction.

Proposal of a Mechanism of the Reaction Cascade Leading to the Metal-Bound Heterocycles. As mentioned above, the reaction of the imido complex **1** with alkyl isocyanides to give the N-heterocyclic fragments coordinated to titanium occurs without detectable intermediates, which implies that the first reaction step is the rate-determining step in this conversion. This situation pertains even if the pyridine-free imidotitanium complex [(κ^3-N$_2$Npy)Ti═NtBu] (**1a**)[15] is employed in these reactions.[15] The first C−N coupling reaction is therefore assumed to be the slow reaction step rather than the displacement of pyridine. Unfortunately, the extreme rapidity of this conversion to the cyclized species even at low temperatures renders the system unsuitable for a kinetic study using conventional methods. The proposed mechanism displayed in Scheme 5 is thus based on the evidence obtained in the reactions described above and by analogy with known reactions of isocyanides.

The first step is thought to be the insertion of an isocyanide group into the imidotitanium unit to give the metal-bonded carbodiimide in **A**. Although no model compound derived from **1** of this first postulated intermediate could be characterized, the existence of such

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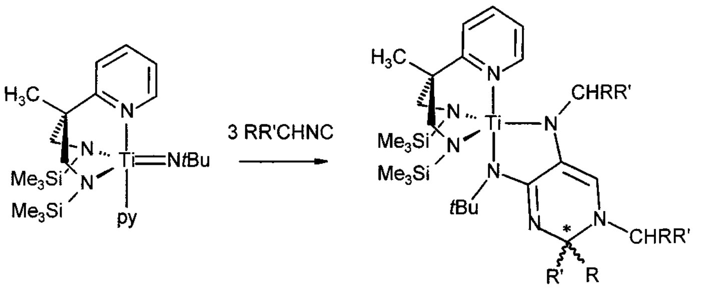
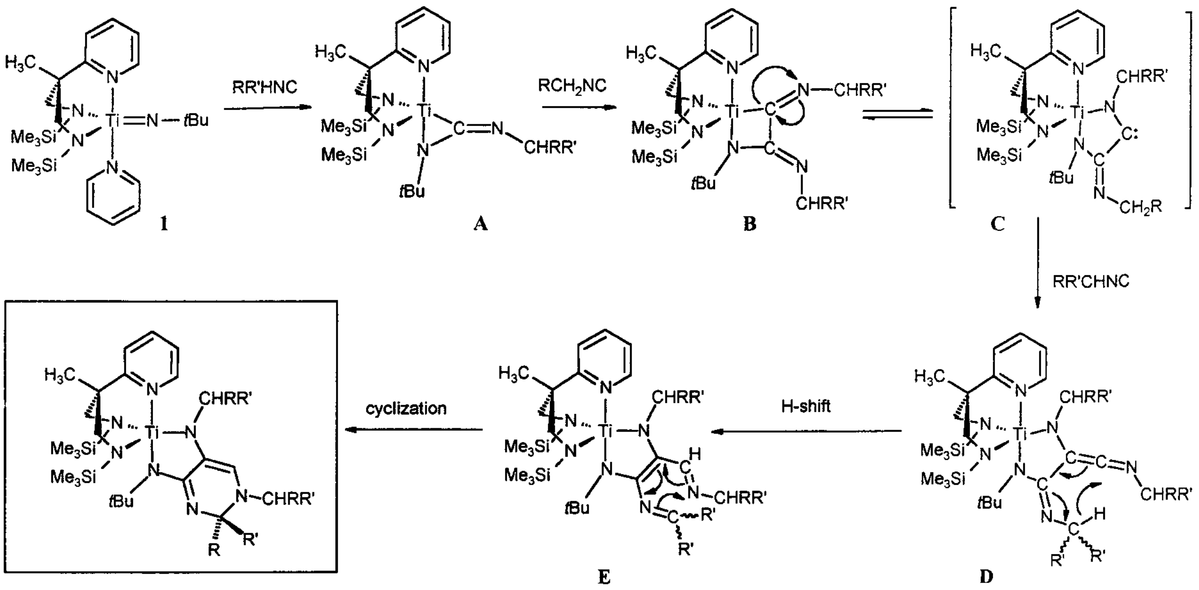
(15) Collier, P. E.; Gade, L. H.; Lloyd, J.; McPartlin, M.; Mountford, P.; Pugh, S. E.; Schubart, M.; Trösch, D. J. M. *Inorg. Chem.* **2000**, in press.

Scheme 4. Reaction of 1 with Secondary Alkyl Isocyanides to Give 5a−c



R, R'	
CH_3, CH_3	**5a**
CH_3, Ph	**5b**
C_5H_{10}	**5c**

Scheme 5. Mechanistic Proposal for the Cascade of C−N and C−C Coupling Reactions of 1 with Isocyanides Giving 4a−d and 5a−c



species has been established by Bergman and co-workers in their study on the reactivity of zirconium and iridium imides toward isocyanides.[8a,b] A rapid successive step is therefore thought to be a second insertion of an isocyanide to give four-membered titanacycle **B**. This proposed intermediate is structurally analogous to complex **2** discussed earlier in this study. The facile conversion of **2** to give the iminoketene derivatives **3a**−**h** leads us to consider a similar transformation in the reaction cascade presented in Scheme 5 (giving **D**). This reaction might occur via a short-lived carbene intermediate, **C**, for which we were unable to obtain direct evidence. However, in view of the well-established chemistry of Arduengo's carbenes[16] as well as the known reaction of carbenes and carbenoids with isocyanides to give iminoketenes,[17] this appears to us to be a reasonable assumption.

The isolation of compounds **3a**−**h** was probably achieved due to the absence of an N-bonded α-CH unit at the imino group. In the presence of a hydrogen atom in this position, a sigmatropic H-shift occurs generating a metal-bound 1,5-diazahexatriene **E**, which undergoes ring closure to give the N-heterocyclic structure in **4a**−**d** and **5a**−**c**. The intermediate **E**, in which one of the tetrahedral α-carbon centers of an isocyanide is planarized, also explains the observation of a mixture of diastereomers in the reaction of **1** with $Ph(CH_3)CHNC$ to give **5c**. The latter rearrangement of in situ generated imidoylketimines to dihydropyrimidines is a known conversion that may be used in the synthesis of certain dihydropyrimidine derivatives.[18]

The cascade of reactions discussed here is an example of the complicated but selective conversions that isocyanides may undergo with early transition metal amides. A notable example from the literature of an imide−isocyanide coupling sequence leading to a metal-bonded N-heterocyclic system was reported by Wilkinson and co-workers, who studied the reactivity of transient $[Cp^*Cr{=}N(2,6\text{-}i\text{Pr}_2C_6H_3)]$ toward isocyanides resulting in a coordinated amino-functionalized dihydroquinoline.[8c]

Conclusions

The imidotitanium complex **1** undergoes single or multiple coupling reactions with isocyanides. It has been possible to structurally characterize the principle types of products obtained in these reactions. The most interesting conversion is certainly the reaction cascade leading to metal-bound diamino dihydropyrimidines and

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[16] Arduengo, A. J., III; Bock, H.; Chen, H.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641, and references therein.

[17] Krow, G. R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435. (b) Flowers, W. T.; Haszeldine, R. N.; Owen, C. R.; Thomas, A. *J. Chem. Soc., Chem. Commun.* **1974**, 134. (c) Ciganek, E. *J. Org. Chem.* **1970**, *35*, 862. (d) Boyer, J. H.; Beverung, W. *J. Chem. Soc., Chem. Commun.* **1969**, 1377. (e) Green, J. A.; Singer, L. A. *Tetrahedron Lett.* **1969**, 5093. (f) Obata, N.; Takizawa, T. *Tetrahedron Lett.* **1969**, 3403.

[18] Goerdeler, J.; Lindner, C.; Zander, F. *Chem. Ber.* **1981**, *114*, 536.

their homologs in the absence of any byproducts. This not only provides an alternative to established syntheses of this class of N-heterocycles[18] but offers the opportunity of further functionalizations of the organic product. Work toward this aim is currently under way.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze−pump−thaw" cycles and dried over 4 Å molecular sieves. Solids were separated from suspensions by centrifugation, thus avoiding filtration procedures. The centrifuge employed was a Rotina 48 (Hettich Zentrifugen, Tuttlingen, Germany), which was equipped with a specially designed Schlenk tube rotor.[19]

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable-temperature unit (at 200.13, 50.32, and 39.76 MHz, respectively) with tetramethylsilane as references. Infrared spectra were recorded on Perkin-Elmer 1420 and Bruker IRS 25 FT-spectrometers.

Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at the University of Würzburg. The imidotitanium complex [(κ^3-N_2Npy)Ti(=N*t*Bu)(py)] (**1**) was prepared as previously reported by us.[6] The isocyanides were prepared according to synthetic procedures reported in the literature.[20] All other chemicals used as starting materials were obtained commercially and used without further purification.

(1) Preparation of [(κ^3-N_2Npy)Ti[N(tBu)C(=N-2,6-$Me_2C_6H_3$)C(=N-2,6-$Me_2C_6H_3$)] (2). A suspension of compound **1** (1.00 g = 1.98 mmol) and 2,6-$C_6H_3(CH_3)_2$NC (550 mg = 4.19 mmol) in benzene (5 mL) was stirred for 10 min and then centrifuged for 15 min at 2000 rpm. The liquid phase was separated from the residue, which was resuspended in 3−4 mL of benzene and centrifuged. The solvent was then separated from the residue, which was dried in vacuo. Compound **2** is a dark brown microcrystalline powder that can be recrystallized from thf. Yield: 75%; mp 24 °C. Anal. Calcd for $C_{37}H_{56}N_6Si_2Ti$ [688.94]: C, 64.51; H, 8.19; N, 12.20. Found: C, 63.62; H, 7.97; N, 12.09. IR (Nujol): 1599 m, 1580 m, 1572 s, 1521 vw, 1463 s, 1377 m, 1295 w, 1243 m, 1204 m, 1186 w, 1186 w, 1085 w, 1031 m, 945 vw, 918 w, 867 s, 832 m, 789 w, 772 w, 754 w, 727 vw, 645 vw, 602 vw cm^{-1}. ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ 0.08 [s, 18 H, Si$(CH_3)_3$], 0.90 (s, 3 H, CCH_3), 2.02 [s, 9 H, $C(CH_3)_3$], 2.09 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 2.64 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 3.02 (d, $^2J_{HH}$ = 13.0 Hz, 2 H, C*H*HN), 3.63 (d, CH*H*N), 6.14 (m, 1 H, H^3), 6.62 (m, 1 H, H^5), 6.62 (m, 1 H, Lig.−CH), 6.73 [d, br, $^3J_{HH}$ = 10 Hz, 4 H, 2H $H^{3,5}$ of 2,6-$C_6H_3(CH_3)_2$], 6.94 [t, br, 2 H, 2H H^4 of 2,6-$C_6H_3(CH_3)_2$], 7.19 (m, 1 H, Lig.-CH) 7.41 (m, 1 H, H^6). {^{1}H}^{13}C NMR (100.6 MHz, C_6D_6, 295 K): δ 0.0 [Si$(CH_3)_3$], 19.2 [2,6-$C_6H_3(CH_3)_2$], 20.0 [2,6-$C_6H_3(CH_3)_2$], 22.9 (CCH_3), 30.0 [$C(CH_3)_3$], 48.0 (CCH_3), 58.9 [$C(CH_3)_3$], 63.4 (CH_2N), 118.9 (CH), 119.6 (CH), 120.9 (C^3), 121.7 (C^5), 126.9 (CH), 127.7 (CH), 128.4 (C), 128.7 (C), 138.3 (C^4), 147.2 (C^6), 151.6 (C), 151.8 (C), 152.3 (C), 158.5 (C^2), 212.5 (C). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 2.97.

(2) General Procedure for the Synthesis of [(κ^3-N_2Npy)-Ti{N(*t*Bu)C[N(2,6-$Me_2C_6H_3$)]C(=C=NR)N(2,6-$Me_2C_6H_3$)] (R = Et, 3a; *n*Bu, 3b; *i*Pr, 3c; Cy, 3d; *t*Bu, 3e; $PhCH_2$, 3f; *p*-Tol, 3g; (R)-CH(CH_3)Ph, 3h). Complex **2** (200 mg) was suspended in 5 mL of benzene and 1.2 molar equiv of the respective isocyanide was added to the stirred suspension. The reaction was monitored by ^{1}H NMR spectroscopy, and the mixture was worked up after complete conversion was observed (EtNC, *n*BuNC 5 min, *i*PrNC 30 min, CyNC, BzNC, $C_6H_5CH(CH_3)$-NC 45 min, *p*-TolNC *t*BuNC overnight). The solvent and excess isocyanide were removed in vacuo; subsequently, the residue was triturated with 2−4 mL of pentane and centrifuged for 10 min at 2000 rpm. The solid thus obtained was isolated and dried in vacuo. Compounds **3a**−**h** are brown powders that can be recrystallized from toluene at −35 °C. Crystals could also be obtained from the solutions in pentane at −35 °C.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(=C=NEt)N-(2,6-$Me_2C_6H_3$)]}] (3a). Yield: 71%; mp 46 °C. Anal. Calcd for $C_{40}H_{61}N_7Si_2Ti$ [744.02]: C, 64.57; H, 8.26; N, 13.18. Found: C, 64.80; H, 7.90; N, 12.12. IR (Nujol): 1976 s, 1599 w, 1552 vs, 1463 vs, 1373 m, 1272 m, 1245 s, 1202 m, 1140 w, 1089 w, 1034 s, 1011 w, 930 m, 910 m, 894 w, 863 vs, 832 s, 785 m, 676 w, 599 w cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 295 K): δ 0.19 [Si$(CH_3)_3$], 0.54 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.02 (s, 3 H, CCH_3), 2.17 [s, 9 H, $C(CH_3)_3$], 2.35 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 2.64 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 2.64 (q, 2 H, CH_2CH_3), 3.11 (d, $^2J_{HH}$ = 12.9 Hz, 2 H, C*H*HN), 4.03 (d, 2 H, CH*H*N), 6.20 (m, 1 H), 6.72 − 6.95 (m, b, 7 H), 7.12 (s, 1 H). {^{1}H}^{13}C NMR (100.6 MHz, C_6D_6, 295 K): δ 1.0 [Si$(CH_3)_3$], 14.9 (CH_3), 19.9 [2,6-$C_6H_3(CH_3)_2$], 21.2 [2,6-$C_6H_3(CH_3)_2$], 24.2 (CCH_3), 31.8 [$C(CH_3)_3$], 48.3 (CCH_3), 49.0 (CH_2CH_3), 51.2 [$C(CH_3)_3$], 64.8 (CH_2N), 102.3 (*C*=C=N), 120.0, 120.4, 121.4, 125.2, 136.0, 138.0, 147.2, 151.4, 151.6, 159.0, 161.5, 193.1 (C=*C*=N). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 4.0.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(=C=N*n*Bu)N-(2,6-$Me_2C_6H_3$)]}] (3b). Yield: 298 mg (63%); mp 46 °C. Anal. Calcd for $C_{40}H_{61}N_7Si_2Ti$ [772.08]: C, 65.34; H, 8.49; N, 12.70. Found: C, 65.39; H, 8.49; N, 12.61. IR (Nujol): 1969 s, 1599 w, 1556 s, 1459 vs, 1373 m, 1264 w, 1245 m, 1198 w, 1085 w, 1034 w, 937 w, 918 m, 887 m, 855 s, 836 m, 789 m, 766 vw, 750 vw, 599 w cm^{-1}. ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ 0.2 [Si$(CH_3)_3$], 0.74 [t, $^3J_{HH}$ = 6.1 Hz, 3 H, $(CH_2)_3CH_3$], 0.86−0.98 [m, b, 4 H, $CH_2(CH_2)_2CH_3$], 1.02 (s, 3 H, CCH_3), 2.16 [s, 9 H, $C(CH_3)_3$], 2.36 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 2.60−2.67 (m, C=C=N−CH_2), 2.64 [s, 2,6-$C_6H_3(CH_3)_2$], 3.11 (d, $^2J_{HH}$ = 12.8 Hz, 2 H, C*H*HN), 4.03 (d, 2 H, CH*H*N), 6.20 (m, 1 H, H^3), 6.76−6.93 (m, b, 8 H, aromatic CH). {^{1}H}^{13}C NMR (100.6 MHz, C_6D_6, 295 K): δ 1.08 [Si$(CH_3)_3$], 19.9 [2,6-$C_6H_3(CH_3)_2$], 20.5 [CH_3], 21.2 [2,6-$C_6H_3(CH_3)_2$], 24.2 (CCH_3), 31.9 [$C(CH_3)_3$], 32.3 (CH_2), 48.3 (CCH_3), 54.0 (C=NCH_2), 62.0 ($C(CH_3)_3$), 64.9 (CH_2N), 101.7 (*C*=C=N), 120.0, 120.3, 121.4, 134.2, 136.0, 147.2, 151.5, 151.6, 159.0, 161.5, 193.6 (C=*C*=N). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 4.0.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(=C=N*i*Pr)N-(2,6-$Me_2C_6H_3$)]}] (3c). Yield: 77%; mp 52 °C. Anal. Calcd for $C_{41}H_{63}N_7Si_2Ti$ [758.05]: C, 64.96; H, 8.38; N, 12.93. Found: C, 61.56; H, 8.15; N, 12.07. IR (Nujol, NaCl): 1982 s, 1965 w, 1601 vw, 1559 s, 1461 vs, 1377 s, 1299 vw, 1260 s, 1245 s, 1203 w, 1166 w, 1090 s, 1033 s, 943 w, 916 w, 891 w, 862 s, sh, 836 s, 807 s cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 295 K): δ 0.19 [s, 18 H, Si$(CH_3)_3$], 0.59 [d, $^3J_{HH}$ = 3.2 Hz, 6 H, $CH(CH_3)_2$], 1.03 (s, 3 H, CCH_3), 2.15 (s, 9H, *t*Bu), 2.34, 2.63 [2H s, 2H 6 H, 2,6-$C_6H_3(CH_3)_2$], 2.92 [sep, 1 H, $CH(CH_3)_2$], 3.12 (d, $^2J_{HH}$ = 12.8 Hz, 2 H, C*H*HN), 4.02 (d, 2 H, CH*H*N) 6.20 (m, 1 H, H^5), 6.75−7.12 (m, 9 H, aromatic CH). {^{1}H}^{13}C NMR (100.6 MHz, C_6D_6, 295 K): δ 1.0 [s, 18 H, Si$(CH_3)_3$], 14.2 [$C(CH_3)_3$], 19.9 [2,6-$C_6H_3(CH_3)_2$], 21.2 [2,6-$C_6H_3(CH_3)_2$], 22.6 [$CH(CH_3)_2$], 24.2 (CCH_3), 48.2 (CCH_3), 54.9 [$CH(CH_3)_2$], 61.2 [$C(CH_3)_2$], 64.7 (CH_2N), 103.4 (*C*=C=N), 119.9, 120.2, 121.2, 125.1, 128.7 (CH), 136.3 (C), 137.8 (C^4), 147.2 (C^6), 151.1, 151.2, 158.8, 161.5 (C), 189.7 (C=*C*=N). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 3.65.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(=C=NCy)N-(2,6-$Me_2C_6H_3$)]}] (3d). Yield: 75%; mp 110 °C. Anal. Calcd for $C_{44}H_{67}N_7Si_2Ti$ [806.09]: C, 66.30; H, 8.35; N, 12.30.

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(19) Hellmann, K. W.; Gade, L. H. *Verfahrenstechnik* **1997**, *31* (5), 70.

(20) Ugi, I.; Meyr, R. *Org. Synth.* **1961**, *41*, 300. (b) Ugi, I.; Meyr, R. *Org. Synth.* **1961**, *41*, 1060.

Found: C, 65.79; H, 8.44; N, 11.23. IR (Nujol): 1973 s, 1601 vw, 1551 s, 1462 vs 1377 s, 1250 s, 1233 w, 1191 w, 1167 vw, 1089 w, 1061 vw, 1035 s, 935 vw, 914 vw, 902 vw, 892 vw, 862 s, 836 w, 811 vw, 811 vw, 785 vw, 776 vw, 758 vw, 605 s cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6, 295 K): δ 0.20 (s, 18 H, $SiMe_3$), 0.8−1.6 (m, br, 10 H, 5H CH_2), 1.02 (s, 3 H, CCH_3), 2.10 (s, 9 H, *t*Bu), 2.37 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 2.59 (m, 1 H, N−CH), 2.65 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 3.12 (d, $^2J_{HH}$ = 12.9 Hz, 2 H, C*H*HN), 4.02 (d, 2 H, CH*H*N), 6.21 (m, 1 H, H^5), 6.60−6.95 (m, 8 H, aromatic CH), 7.19 (1 H, CH). {^{1}H}^{13}C NMR (50.3 MHz, C_6D_6, 295 K): δ 1.0 [$Si(CH_3)_3$], 19.9 (CH_2), 21.3 (CH_2), 22.7 (CH_3), 24.2 (CCH_3), 25.3 (CH_2), 26.1 (CH_3), 33.2 [$C(CH_3)_3$], 48.2 (CCH_3), 61.2 [$C(CH_3)_3$], 62.1 (N−CH), 64.8 (CH_2N), 102.8 (*C*═C═N), 119.9 (CH), 120.0 (CH), 121.2 (CH), 125.2 (CH); 128.5 (CH), 128.7 (CH), 136.3 (C), 137.9 (CH), 147.2 (C^6), 151.2 (C), 151.3 (C), 158.9 (C), 161.6 (C), 190.3 (C═*C*═N). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 3.9.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(═C═N*t*Bu)N-(2,6-$Me_2C_6H_3$)]}] (3e). Yield: 77%; mp 100 °C. Anal. Calcd for $C_{42}H_{65}N_7Si_2Ti$ [772.08]: C, 65.39; H, 8.49; N, 12.70. Found: C, 65.79; H, 8.52; N, 12.06. IR (Nujol): 1967 w, 1601 vw, 1553 w, 1458 vs, 1377 s, 1246 w, 1200 vw, 1088 vw, 1033 w, 941 vw, 920 vw, 890 vw, 859 w, 837 vw, 805 vw, 785 vw, 756 vw, 723 vw cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 295 K): δ 0.19 [$Si(CH_3)_3$], 0.66 [s, 9 H, C═C═N$C(CH_3)_3$], 1.04 (s, 3 H, CCH_3), 2.13 (s, 9 H, N*t*Bu), 2.35, 2.62 [2,6-$C_6H_3(CH_3)_2$], 3.12 (d, $^2J_{HH}$ = 12.6 Hz, 2 H, C*H*HN), 4.01 (d, 2 H, CH*H*N), 6.22 (H^5), 6.67−7.13 (m, 9 H, aromatic CH). {^{1}H}^{13}C NMR (50.3 MHz, C_6D_6, 295 K): δ 0.9 [$Si(CH_3)_3$], 20.0 [2,6-$C_6H_3(CH_3)_2$], 21.3 [2,6-$C_6H_3(CH_3)_2$], 24.2 (CCH_3), 29.5 [═C═N$C(CH_3)_3$], 32.0 [N$C(CH_3)_3$], 48.3 (CCH_3), 60.0 [$C(CH_3)_3$], 61.2 [$C(CH_3)_3$], 64.7 (CH_2N), 104.0 (*C*═C═N), 119.9, 120.0, 121.1, 125.1, 128.1, 128.9 (CH), 136.4 (C), 137.8 (CH), 147.3 (C^6), 150.6, 150.8, 158.3, 161.6 (C), 187.1 (C═*C*═N). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 3.9.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(═C═NCH_2Ph)N(2,6-$Me_2C_6H_3$)]}] (3f). Yield: 76%; mp 44 °C. Anal. Calcd for $C_{44}H_{67}N_7Si_2Ti$ [798.11]: C, 67.05; H, 7.88; N, 12.16. Found: C, 65.69; H, 7.81; N, 11.81. IR (Nujol): 1957 s, 1600w, 1553 s, 1460 vs, 1263 s, 1247 s, 1197 w, 1093 w, 1047 w, 1030 m, 913 w, 887 w, 860 m, 833 m, 810 w cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6, 295 K): δ 0.18 [s, 18 H, $Si(CH_3)_3$], 1.03 (s, 3 H, CCH_3), 2.15 (s, 9 H, N*t*Bu), 2.29 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 2.64 [s, 6 H, 2,6-$C_6H_3(CH_3)_2$], 3.10 (d, $^2J_{HH}$ = 12.8 Hz, 2 H, C*H*HN), 3.80 (s, 2 H, $CH_2C_6H_5$), 4.02 (d, 2 H, CH*H*N), 6.18 (m, 1 H, H^5), 6.72−7.15 (m, 14 H, aromatic CH). {^{1}H}^{13}C NMR (50.3 MHz, C_6D_6, 295 K): δ 1.0 [$Si(CH_3)_3$], 19.7 [2,6-$C_6H_3(CH_3)_2$], 21.0 [2,6-$C_6H_3(CH_3)_2$], 24.1 (CCH_3), 31.7 [$C(CH_3)_3$], 48.3 (CCH_3), 57.6 ($CH_2C_6H_5$), 61.2 ($C(CH_3)$, 64.8 (CH_2N), 102.6 (*C*═C═N), 120.0, 120.4, 121.3, 125.2, 126.6, 128.0, 128.2, 128.3, 128.8 (CH), 135.6 (C), 138.0 (CH), 138.9 (C), 147.0 (CH), 151.2, 151.3, 158.7, 161.3 (C), 197.2 (C═*C*═N). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 3.8.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(═C═N*p*-Tol)N-(2,6-$Me_2C_6H_3$)]}] (3g). Yield: 75%; mp 46 °C. Anal. Calcd for $C_{45}H_{63}N_7Si_2Ti$ [806.09]: C, 67.05; H, 7.88; N, 12.16. Found: C, 66.29; H, 7.82; N, 11.02. IR (Nujol): 1954 vw, 1552 w, 1458 vs, 1377 s, 1277 w, 1255 w, 1204 vw, 1090 vw, 1032 w, 940 vw, 916 vw, 860 w, 835 vw, 722 vw cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6, 295 K): δ 0.24 [s, 18 H, $Si(CH_3)_3$], 1.02 (s, 3 H, C_6H_4−CH_3), 1.96, (s, 3 H, CCH_3), 2.21 (s, 9 H, tBu), 2.40 (s, 6, 2,6-$C_6H_3(CH_3)_2$), 2.66 (s, 6 H, 2,6-$C_6H_3(CH_3)_2$), 3.12 (d, $^2J_{HH}$ = 12.8 Hz, 2 H, C*H*HN), 4.04 (d, 2 H, CH*H*N), 6.17 (m,1 H, H^5), 6.57−6.95 (m, 13 H, aromatic protons). {^{1}H}^{13}C NMR (50.3 MHz, C_6D_6, 295 K): δ 1.1 [$Si(CH_3)_3$], 19.9 [2,6-$C_6H_3(CH_3)_2$], 21.0 (C_6H_4−CH_3), 21.2 [2,6-$C_6H_3(CH_3)_2$], 24.1 (CCH_3), 31.6 [NC-$(CH_3)_3$], 48.3 (CCH_3), 61.3 [N$C(CH_3)_3$], 64.9 (CH_2N), 105.0 (*C*═C═N), 120.0, 121.3, 121.4 [2H C^4 of 2,6-$C_6H_3(CH_3)_2$; C^3], 124.2 [C^{2,6} of *p*-Tol], 125.3 (C^5), 128.3, 128.6, 128.7, 128.8 [2H C^{3,5} of 2,6-$C_6H_3(CH_3)_2$; C,^{4} C^{3,5} of *p*-Tol], 135.5, 135.8 [2H C^{2,6} of 2,6-$C_6H_3(CH_3)_2$], 138.1 (C^4), 141.0 (C^1 of *p*-Tol), 147.1 (C^6), 150.6, 151.5 [2H C^1 of 2,6-$C_6H_3(CH_3)_2$], 159.5 [2,6-C_6H_3-$(CH_3)_2$N*C*], 161.3 (C^2), 200.4 (C═*C*═N) ppm. {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 3.8.

[(κ^3-N_2Npy)Ti[N(*t*Bu)CN(2,6-$Me_2C_6H_3$)]C(═C═NCH-{CH_3}Ph)-N(2,6-$Me_2C_6H_3$)]}] (3h). Yield: 305 mg (73%); mp 50 °C. Anal. Calcd for $C_{46}H_{65}N_7Si_2Ti$ [820.12]: C, 67.37; H, 7.99; N, 11.96. Found: C, 66.63; H, 7.90; N, 11.40. IR (Nujol): 1963 s, 1490 w, 1445 vs, 1350 s, 1278 m, 1188 w, 1145 vs, 1110 w, 1095 m, 1083 m, 1063 w, 1038 vw, 985 m, 960 m, 944 m, 929 s, 846 m, 820 m, 790 w, 754 vs, 732 s, 678 m, 660 m, 595 w, 505 w cm^{-1}. ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ 0.14 [s, 9 H, $Si(CH_3)_3$], 0.24 [s, 9 H, $Si(CH_3)_3$], 0.95 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CHCH_3$), 1.02 (s, 3 H, CCH_3), 2.16 [s, 9 H, $C(CH_3)_3$], 2.31 [s, 3 H, 2,6-$C_6H_3(CH_3)(CH_3)$], 2.33 [s, 3 H, 2,6-$C_6H_3(CH_3)(CH_3)$], 2.60 [s, 3 H, 2,6-$C_6H_3(CH_3)(CH_3)$], 2.66 [s, 3 H, 2,6-$C_6H_3(CH_3)(CH_3)$], 3.05 (d, $^2J_{HH}$ = 12.8 Hz, C*H*HN), 3.17 (d, C*H*HN), 3.92−4.07 (m, 3 H, C*H*CH_3, CH*H*N and CH*H*N), 6.20 (m, 1 H, H^3), 6.72−7.14 (m, 13 H, aromatic protons). {^{1}H}^{13}C NMR (MHz, C_6D_6, 295 K): δ 0.8 [$Si(CH_3)_3$], 1.1 [Si-$(CH_3)_3$], 19.9 [2,6-$C_6H_3(CH_3)(CH_3)$], 20.1 [2,6-$C_6H_3(CH_3)(CH_3)$], 21.2 [2,6-$C_6H_3(CH_3)(CH_3)$], 21.6 [2,6-$C_6H_3(CH_3)(CH_3)$], 23.7 ($CHCH_3$), 24.3 (CCH_3), 31.9 [$C(CH_3)_3$], 48.4 (CCH_3), 61.4 [$C(CH_3)_3$], 62.6 ($CHCH_3$), 64.8 (CH_2N), 64.9 (CH_2N), 104.8 (*C*═C═N), 120.1, 120.3 (2H CH), 121.4 (C^3), 125.3, 125.6, 127.1, 129.8 (je CH), 135.7, 136.8 (2H C), 138.1 (CH), 145.0 (C), 147.3 (CH), 150.9, 151.2, 158.7, 161.5 (4H C), 193.6 (C═*C*═N). {^{1}H}^{29}Si NMR (39.8 MHz, C_6D_6, 295 K): δ 3.9, 4.2.

(3) General Procedure for the Synthesis of Dihydropyrimidine Compounds [(κ^3-N_2Npy)Ti{N*t*Bu}{η^2-NR}-[−C═NCH(R)NRCHC−]] (4a−d). Method a. The imido complex **1** (200 mg, 0.396 mmol) was suspended in the isocyanide with which it was to be reacted and stirred for 15 min. The solvent was then removed in vacuo and the residue triturated with 3−5 mL of cold pentane (0 °C). After storing overnight at −35 °C, the solvent was decanted and the residue dried in vacuo.

Method b. To a solution of **1** (200 mg, 0.396 mmol) in 5 mL of benzene or toluene was added 3 or more equivalents of isocyanide. The reaction mixtures turned from yellow to dark brown. After stirring for the appropriate amount of time (EtNC, *n*BuNC, *i*PrNC: 5−10 min; CyNC, BzNC, C_6H_5CH-(CH_3)NC: 30 min) the solvent, pyridine, and excess isocyanide were removed in vacuo, and the residue was triturated with pentane. After storing at −35 °C overnight, the solvent was decanted from the solid precipitate, which was dried in vacuo.

[(κ^3-N_2Npy)Ti{N*t*Bu}{η^2-NMe}(−C═NCH_2NCH_3CH═C−)] (4a). Yield: 78%. Anal. Calcd for $C_{25}H_{45}N_7Si_2Ti$ [547.73]: C, 54.82; H, 8.28; N, 17.90. Found: C, 54.85; H, 8.21; N, 17.96. IR (benzene): 2940 m, 2870 m, 2840 m, 2810 m, 2770 w, 1625 w, 1595 m, 1575 m, 1530 m, 1465 m, 1428 m, 1358 m, 1240 m, 1142 m, 1054 m, 1040 m, 908 m, 855 m, 774 m, 744 m, 702 m cm^{-1}. ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ −0.05 [s, NSi-$(CH_3)_3$], 1.03 (s, CCH_3), 2.06 [s, $C(CH_3)_3$], 2.48 (s, TiNCH_3), 3.04 (d, $^2J_{HH}$ = 12.9 Hz, C*H*HNSi), 3.25 (s, NCH_3), 3.91 (d, CH*H*NSi), 4.86 (s, CH_2), 5.45 (s, CH), 6.54 (ddd, H^5), 6.84 (ddd, H^3, $^3J_{HH}$ = 7.9 Hz), 7.05 (dt, H,^{4} $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz), 8.44 (ddd, H,^{6} $^3J_{HH}$= 5.5 Hz, $^4J_{HH}$= 1.5 Hz). {^{1}H}^{13}C NMR (C_6D_6, 295 K): δ −0.5 [$NSi(CH_3)_2$], 22.9 (CCH_3), 30.1 [$C(CH_3)_3$], 40.6, 40.7 (NCH_3 and TiNCH_3), 48.3 (CCH_3), 58.7 [$C(CH_3)_3$], 64.0 (CH_2NSi), 70.3 (CH_2-ring), 117.2 (C_4N_2−CH), 120.6 (C^3), 121.3 (C^5), 129.3 (C_4N_2), 134.9 (C_4N_2), 138.1 (q−C), 146.9 (C^6), 160.6 (C^2), 162.8 (C_4N_2−*C*═N).

[(κ^3-N_2Npy)Ti{NtBu}{η-NEt}[−C═NCHCH_3N(CH_2-CH_3)═C−]] (4b). Yield: 76%; mp 16 °C (dec). Anal. Calcd for $C_{28}H_{53}N_7Si_2Ti$ [591.83]: C, 56.83; H, 9.03; N, 16.57. Found: C, 54.64; H, 8.53; N, 15.64. IR (Nujol, KBr): 1461 s, 1377 s, 1245 w, 1091 w, 1920 w, 832 w, 803 w cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 295 K): δ −0.51 [s, 9 H, $Si(CH_3)_3$], −0.1 [s, 9 H, $Si(CH_3)_3$], 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3, N$^{3'}$−CH_2CH_3), 1.17

(s, b, 3 H, CCH$_3$), 1.30 (t, J_{vic} = 6.9 Hz, 3 H, Ti−N−CH$_2$C*H*$_3$), 1.64 (d, $^3J_{\mathrm{HH}}$ = 6.1 Hz, 3 H, CHC*H*$_3$), 1.94 (s, 3 H, CH$_3$), 2.90 (q, 2 H, N$^{3'}$−C*H*$_2$CH$_3$), 3.15 (d, $^2J_{\mathrm{HH}}$ = 12.6 Hz, C*H*HN), 3.21 (d, C*H*HN), 3.74 (q, 1 H, Ti−N−C*H*HCH$_3$), 3.80 (q, 1 H, Ti−N−CH*H*CH$_3$), 3.88 (d, 1 H, CH*H*N), 3.94 (d, 1 H, CH*H*N), 5.06 (dq, $^5J_{\mathrm{H^{2'}H^{4'}}}$ = 0.9 Hz, 1 H, H$^{2'}$), 5.42 (d, 1 H, H$^{4'}$), 7.0 (d, $J_{\mathrm{H^3H^4}}$ = 8.0 Hz, 1 H, H^3), 7.10 (dd, $J_{\mathrm{H^5H^4}}$ = 7.6 Hz, $J_{\mathrm{H^5-H^6}}$ = 5.4 Hz, 1 H, H^5), 7.22 (ddd, $J_{\mathrm{H^4H^6}}$ = 1.7 Hz, 1 H, H^4), 8.66 (ddd, $J_{\mathrm{H^6H^3}}$ = 1.1 Hz, 1 H, H^6). {^{1}H}^{13}C NMR (100.6 MHz, C$_6$D$_6$, 295 K): δ −0.2 [Si(CH$_3$)$_3$], −0.1 [Si(CH$_3$)$_3$], 14.6 (CH$_2$*C*H$_3$), 17.0 (CH$_2$*C*H$_3$), 21.5 (CH$_2$*C*H$_3$), 23.5 (C*C*H$_3$), 30.3 (C(*C*H$_3$)$_3$), 46.7 (*C*H$_2$CH$_3$), 47.8 (*C*H$_2$CH$_3$), 48.9 (*C*CH$_3$), 58.9 (*C*(CH$_3$)$_3$), 64.1 (CH$_2$N), 64.3 (CH$_2$N), 70.7 (C$^{2'}$), 114.6 (C$^{4'}$), 121.0 (C^3), 121.4 (C^5), 130.8 (C$^{5'}$), 138.2 (C^6), 161.2 (C^2), 161.6 (C$^{6'}$). {^{1}H}^{29}Si NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ 0.17, 1.19.

[(κ^3-N$_2$Npy)Ti{NtBu}{η-N*n*Bu}[−C=NCH(C$_3$H$_7$)N(C$_4$H$_7$)−CH=C−]] (4c). Yield: 67%; mp 35 °C. Anal. Calcd for C$_{34}$H$_{65}$N$_7$Si$_2$Ti [675.99]: C, 60.41; H, 9.69; N, 14.50. Found: C, 60.95; H, 9.22; N, 14.04. IR (Nujol): 1629 vw, 1594 vw, 1460 s, 1375 s, 1258 w, 1243 w, 1097 w, 1018 w, 833 w, 798 w, 719 w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 295 K): δ −0.01 [Si(CH$_3$)$_3$], 0.07 [Si(CH$_3$)$_3$], 0.88 (t, J = 7.3 Hz, 3 H, CH$_3$), 0.94 (t, J = 7.3 Hz, 3 H, CH$_3$), 1.08 (s, b, 3 H, CCH$_3$), 1.13 (t, J = 7.3 Hz, 3 H, CH$_3$), 1.18−1.45 (m, b, 6 H, 3 H C*H*$_2$CH$_3$), 1.5−2.2 (m, b, 6 H, 3 H CH$_2$), 2.00 [s, 9 H, C(CH$_3$)$_3$], 2.95 (m, 1 H, N$^{3'}$C*H*HCH$_2$-CH$_2$CH$_3$), 2.99 (m, 1 H, N$^{3'}$CH*H*CH$_2$CH$_2$CH$_3$), 3.09 (d, $^2J_{\mathrm{HH}}$ = 12.6 Hz, C*H*HN), 3.22 (dd, 1 H, CH*H*N), 3.65 (m, b, 1 H, C$^{2'}$HC*H*HCH$_2$CH$_3$), 3.81 (m, b, 1 H, C$^{2'}$HCH*H*CH$_2$CH$_3$), 3.88 (d, $^2J_{\mathrm{HH}}$ = 12.6 Hz, C*H*HN), 3.95 (d, 1 H, CH*H*N), 4.98 (dt, $^4J_{\mathrm{H^{2'}H^{4'}}}$ = 1.2 Hz, $^3J_{\mathrm{HH}}$ = 5.9 Hz, 1 H, H$^{2'}$), 5.54 (d, 1 H, H$^{4'}$), 6.60 (m 1 H, H^3), 6.95−7.14 (m, 2 H, H,^{4} H^5), 8.70 (m, 1 H, H^6). {^{1}H}^{13}C NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ −0.1 [Si(CH$_3$)$_3$], 1.4 [Si(CH$_3$)$_3$], 14.3 (CH$_3$), 14.5 (CH$_3$), 14.9 (CH$_3$), 19.9 (CH$_2$), 20. (CH$_2$), 21.5 (CH$_2$), 23.4 (CCH$_3$), 30.1 [C(*C*H$_3$)$_3$], 49.0 (*C*CH$_3$), 53.7 (CH$_2$), 54.4 (CH$_2$), 59.0 [*C*(CH$_3$)$_3$], 64.0 (CH$_2$N), 64.2 (CH$_2$N), 74.9 (C$^{2'}$), 115.0 (C$^{4'}$), 120.7 (C^3), 121.1 (C^5), 131.1 (C$^{5'}$), 137.8 (C^6), 146.9 (C^4), 161.2, 161.4 (C^2, C$^{6'}$). {^{1}H}^{29}Si NMR (39.8 MHz, C$_6$D$_6$, 295 K): δ 1.5.

[(κ^3-N$_2$Npy)Ti{N*t*Bu}{η-NCH$_2$Ph}[−C=NCH(C$_6$h$_5$)N-(CH$_2$Ph)CH=C−]] (4d). Yield: 56%; mp 24 °C (dec). Anal. Calcd for C$_{43}$H$_{59}$N$_7$Si$_2$Ti [778.93]: C, 66.38; H, 7.64; N, 12.60. Found: C, 65.43; H, 7.24; N, 11.96. IR (Nujol, KBr): 1459 s, 1379 s, 1243 vw, 918 vw, 833 w, 741 w, 697 w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 295 K): δ −0.28 [s, 9 H, Si(CH$_3$)$_3$], 0.08 [s, 9 H, Si(CH$_3$)$_3$], 1.22 (s, 3 H, CH$_3$], 2.06 [C(CH$_3$)$_3$], 2.94 (d, $^2J_{\mathrm{HH}}$ = 12.7 Hz, 1 H, C*H*HN), 3.13 (d, 2 H, CH*H*N), 3.80 (s, b, 2 H, Ti−N−C*H*$_2$−C$_6$H$_5$), 3.93 (d, $^2J_{\mathrm{HH}}$ = 13.4 Hz, 1 H, C*H*HN), 3.99 (d, 1 H, CH*H*N), 4.79 (d, $^2J_{\mathrm{HH}}$ = 14.7 Hz, 1 H, N$^{3'}$-C*H*H−C$_6$H$_5$), 5.03 (d, H, N$^{3'}$-CH*H*-C$_6$H$_5$), 5.31 (s, 1 H, H$^{4'}$), 6.08 (s, 1 H, H$^{2'}$), 6.15 (m, 1 H, H^3), 6.70−7.40 (m, aromatic H), 8.02 (m, 2 H, aromatic H), 8.54 (m, 1 H, H^6). {^{1}H}^{13}C NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ −0.5 [Si(CH$_3$)$_3$], −0.2 [Si(*C*H$_3$)$_3$], 23.1 (C*C*H$_3$), 48.6 (*C*CH$_3$), 53.4 (*C*H$_2$C$_6$H$_5$), 56.6 (*C*H$_2$C$_6$H$_5$), 59.5 [*C*(CH$_3$)$_3$], 64.1 (CH$_2$N), 64.5 (*C*H$_2$N), 76.6 (C$^{2'}$), 115.8 (C$^{4'}$), 120.6 (CH), 121.3 (CH), 123.6 (CH), 126.4 (CH), 126.5 (CH), 126.7 (CH), 127.2 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.8 (CH), 129.0 (CH), 135.4 (CH), 138.3 (CH), 146.0 (C), 147.0 (CH), 148.9 (CH), 149.6 (C), 150.4 (CH), 152.5 (C), 160.4 (C), 161.7 (C), 167.2 (C^2). {^{1}H}^{29}Si NMR (39.8 MHz, C$_6$D$_6$, 295 K): δ 2.4, 2.8.

(4) General Procedure for the Synthesis of Dihydropyrimidine Compounds [(κ^3-N$_2$Npy)Ti{N*t*Bu}{η^2-NR}-[−C=NC(R′)(R″)NRCHC−]] (5a−c). Compounds **5a−c** were synthesized according to method b descibed above. The workup and isolation was entirely analogous.

[(κ^3-N$_2$Npy)Ti{N*t*Bu}{η-N*i*Pr}[−C=NC(CH$_3$)$_2$N(iPr)-CH=C−]] (5a). Yield: 73%; mp 46 °C. Anal. Calcd for C$_{39}$H$_{59}$N$_7$Si$_2$Ti [730.00]: C, 64.17; H, 8.15; N, 13.43. Found: C, 63.98; H, 8.09; N, 13.25. IR (Nujol, KBr): 1629 vw, 1590 vw, 1570 vw, 1511 vw, 1460 s, 1375 s, 1247 vw, 1169 vw, 1113 vw, 837 w, 743 vww, 719 vw cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 295 K): δ 0.27 (s, 18 H [Si(CH$_3$)$_3$], 0.75 [d, $^3J_{\mathrm{HH}}$ = 6.3 Hz, 6 H, TiNCH(C*H*$_3$)$_2$], 1.06 [d, J_{vic} = 6.6 Hz, 6 H, N$^{3'}$CH(C*H*$_3$)$_2$], 1.17 (CCH$_3$), 1.74 [s, 6 H, C$^{2'}$(CH$_3$)$_2$], 2.10 [s, 9 H, C(CH$_3$)$_3$], 3.16 [sep, 1 H, TiNC*H*(CH$_3$)$_2$], 3.38 [sep, 1 H, NH$^{3'}$C*H*(CH$_3$)$_2$], 3.96 (d, $^2J_{\mathrm{HH}}$ = 13.1 Hz, C*H*HN), 4.16 (d, 2 H, CH*H*N), 5.39 (s, 1 H, H$^{4'}$, 6.69 (m, 1 H, H^3), 7.07 (m, 1 H, H^5), 7.19 (m, 1 H, H^4), 8.50 (m, 1 H, H^6). {^{1}H}^{13}C NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ 0.8 [Si(CH$_3$)$_3$], 23.8 [TiNCH(*C*H$_3$)$_2$], 28.5 (C*C*H$_3$), 28.4 [N$^{3'}$CH-(*C*H$_3$)$_2$], 29.8 [C(*C*H$_3$)$_2$], 31.4 [C(*C*H$_3$)$_3$], 47.4 [TiN*C*H(CH$_3$)$_2$], 52.2 [N$^{3'}$*C*H(CH$_3$)$_2$], 55.9 (*C*CH$_3$), 58.8 [*C*(CH$_3$)$_3$], 64.1 (CH$_2$N), 72.9 (C$^{2'}$), 111.3 (C$^{4'}$), 119.9 (C$^{5'}$), 121.1, 123.6 (C^3, C^5), 122.1 (C$^{5'}$), 135.8 C,^{6} 150.4 (C^4), 159.1, 164.4 (C^2, C$^{6'}$). {^{1}H}^{29}Si NMR (39.8 MHz, C$_6$D$_6$, 295 K): δ 1.2.

[(κ^3-N$_2$Npy)Ti{N*t*Bu}{η-NC(Me)Ph}[−C=NC(CH$_3$)-(C$_6$H$_5$)N(−R−CH(Me)Ph)CH=C−] (5b). Anal. Calcd for C$_{46}$H$_{65}$N$_7$Si$_2$Ti [820.12]: C, 67.37; H, 7.99; N, 11.96. Found: C, 66.95; H, 8.02; N, 11.89. Yield: 62%; mp 23 °C. IR (Nujol): 1629 w, 1515 w, 1495 w, 1460 w, 1377 w, 1243 w, 916 w, 833 w, 758 w, 718 w, 665 w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 295 K): δ 0.12 [s, 9 H, Si(CH$_3$)$_3$], 0.37 [s, 9 H, Si(CH$_3$)$_3$], 1.10 (CCH$_3$), 1.16 [d, b, $^3J_{\mathrm{HH}}$ = 5.8 Hz, 6 H, 2 H CH(C*H*$_3$)$_2$], 1.77 (s, 3 H, C$^{2'}$CH$_3$)$_,$ 1.89 [s, 9 H, C(CH$_3$)$_3$], 3.80 (d, $^2J_{\mathrm{HH}}$ = 11.0 Hz, 1 H, C*H*HN), 3.82 (d, 1 H, CH*H*N), 3.88 (d, $^2J_{\mathrm{HH}}$ = 12.6 Hz, 1 H, C*H*HN), 4.02 (CH*H*N), 4.22 (q, TiNC*H*CH$_3$), 4.65 (q, N$^{3'}$C*H*CH$_3$), 5.54 (s, 1 H, H$^{4'}$), 6.88−7.35 (m, b, aromatic CH), 7.87−7.91 (m, 2 H, aromatic CH), 8.39 (H^6) (major product). {^{1}H}^{13}C NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ 1.1 [Si(CH$_3$)$_3$], 1.9 [Si(CH$_3$)$_3$], 21.4 (CH$_3$), 23.8 (C*C*H$_3$), 25.9 (CH$_3$), 28.0 (CH$_3$), 34.6 [C(*C*H$_3$)$_3$], 52.2 (*C*CH$_3$), 56.3 [N*C*HCH$_3$C$_6$H$_5$], 59.3 [*C*(CH$_3$)$_3$], 61.7 [N$^{3'}$*C*H-(CH$_3$)(C$_6$H$_5$)], 64.6 (CH$_2$N), 64.7 (CH$_2$N), 77.8 (C$^{2'}$), 116.7 (C$^{4'}$), 121.3, 121.4, 126.4, 126.5, 126.8, 127.1, 127.4, 127.7, 127.8, 128.5, 136.7, 148.6 (CH), 121.6, 147.1, 147.8, 150.3 (C), 157.9, 163.1 (C^2, C$^{6'}$) (major product). {^{1}H}^{29}Si NMR (39.8 MHz, C$_6$D$_6$, 295 K): δ 1.41 [Si(CH$_3$)$_3$], 2.06 [Si(CH$_3$)$_3$].

[(κ^3-N$_2$Npy)Ti{N*t*Bu}{η-NCy}[−C=NC(C$_5$H$_{10}$)N(Cy)-CH=C−]] (5c). Yield: 66%; mp 18 °C. Anal. Calcd for C$_{40}$H$_{71}$N$_7$Si$_2$Ti [754.10]: C, 63.71; H, 9.49; N, 13.00. Found: C, 64.65; H, 9.12; N, 12.62. IR (Nujol, KBr): 1458 s, 1375 s, 1244 w, 836 w, 747 w, 717 w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 295 K): δ 0.34 [s, 18 H, Si(CH$_3$)$_3$], 1.19 (s, 3 H CCH$_3$), 1.71 [s, 9 H, C(CH$_3$)$_3$], 0.60−2.40 (m, CH$_2$ of Cy), 3.98 (d, $^2J_{\mathrm{HH}}$ = 13.2 Hz, 2 H, C*H*HN), 4.23 (d, 2 H, CH*H*N), 5.57 (s, 1 H, H$^{4'}$), 6.61 (m, 1 H, H^3), 7.14−7.20 (m, H,^{4} H^5), 8.49 (m, 1 H, H^6). {^{1}H}^{13}C NMR (MHz, C$_6$D$_6$, 295 K): δ 0.9 [Si(CH$_3$)$_3$], 22.8 (CH$_2$), 23.7 (CH$_2$), 25.0 (CH$_2$), 26.8 (CH$_2$), 27.3 (CH$_2$), 27.9 (C*C*H$_3$), 29.4 [C(CH$_3$)$_3$], 32.7 (CH$_2$), 34.1 (CH$_2$), 34.4 (CH$_2$), 37.2 (CH$_2$), 54.3 (*C*CH$_3$), 56.0 (CH), 58.7 [*C*(CH$_3$)$_3$], 61.8 (CH), 64.1 (CH$_2$N), 73.5 (C$^{2'}$), 110.7 (C$^{4'}$), 121.2 (CH), 121.9 (CH), 123.0 (C), 128.4 (C), 128.4 (CH), 135.5 (CH), 149.2 (CH), 155.3 (C), 164.5 (C^2). {^{1}H}^{29}Si NMR (50.3 MHz, C$_6$D$_6$, 295 K): δ 1.40.

X-ray Crystallographic Studies of 2, 3d, 3f, 3g, and 4a. Data Collection for 2, 3d, 3f, 3g, and 4a. Crystals of **2**, **3d**, **3f**, **3g**, and **4a** were mounted on a quartz fiber in Lindemann capillaries under argon and in an inert oil. X-ray intensity data were collected with graphite-monochromated radiation, on a Bruker P4 four-circle diffractometer. Details of data collection, refinement, and crystal data are listed in Table 3; the only crystals of **2**, **3f**, and **3g** that could be obtained diffracted relatively weakly at high angle. Lorentz−polarization and absorption corrections were applied to the data of all the compounds.

Structure Solution and Refinement for 2, 3d, 3f, 3g, and 4a. For compounds **2**, **3d**, **3f**, **3g**, and **4a** the positions of the titanium, silicon atoms, and some of the other non-hydrogen atoms were located by direct methods. The remain-

Table 3. Crystal Data and Structure Refinement for 2, 3d, 3f, 3g, and 4a

	2·THF	**3d**·C_6H_6	**3f**·C_7H_8	**3g**·C_6H_6	**4a**
empirical formula	$C_{41}H_{64}N_6OSi_2Ti$	$C_{50}H_{73}N_7Si_2Ti$	$C_{52}H_{71}N_7Si_2Ti$	$C_{51}H_{69}N_7Si_2Ti$	$C_{25}H_{47}N_7Si_2Ti$
fw	761.06	876.23	898.24	884.21	549.78
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
space group	$Pna2_1$	$C2/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
unit cell dimens					
a/Å	21.415(5)	20.865(5)	12.684(2)	20.955(3)	10.031(2)
b/Å	11.914(2)	12.6101(13)	13.876(2)	12.483(2)	11.469(1)
c/Å	17.770(3)	39.310(4)	17.077(2)	39.685(5)	15.465(2)
α/deg	90		74.318(9)		94.333(8)
β/deg	90	102.547(11)	70.41(1)	102.34(1)	108.38(1)
γ/deg	90		65.00(2)		111.976(11)
V/Å^3	45333.9(14)	10096(3)	2537.1(6)	10142(2)	1526.4(4)
Z	4	8	2	8	2
D_{calc}/Mg m^{-3}	1.115	1.153	1.176	1.158	1.196
radiation (λ/Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ/mm^{-1}	0.277	0.257	0.257	0.256	0.384
F(000)	1640	3776	964	3792	592
cryst size/mm	0.38 × 0.52 × 0.40	0.46 × 0.48 × 0.46	0.50 × 0.50 × 0.36	0.12 × 0.50 × 0.50	0.48 × 0.52 × 0.60
θ-range/deg	1.90−21.00	1.90−23.00	1.83−22.00	1.91−21.00	1.42−25.00
limiting hkl indices	$-21 < h < 21$, $-12 < k < 12$ $-17 < l < 17$	$-22 < h < 22$, $-13 < k < 13$ $-44 < l < 43$	$-1 < h < 12$ $-13 < k < 14$ $-17 < l < 17$	$-1 < h < 21$, $-1 < k < 12$, $-40 < l < 39$	$-1 < h < 11$, $-13 < k < 12$, $-18 < l < 17$
no. of reflns collected	5053	14470	6935	6481	6353
no. of ind reflns	4852	7032	5898	5227	5348
R_{int}	0.0531	0.0726	0.0414	0.0650	0.0203
max/min transmn	0.31317/0.24979	0.30529/0.27686	0.844087/0.507447	0.780028/0.370177	0.95820/0.61107
refinement method	full matrix least-squares on F^2	full matrix least-squares on F^2	full matrix least-squares on F^2	full matrix least-squares on F^2	full matrix least-squares on F^2
no. of data/restraints/params	4852/25/491	7032/0/541	5898/0/526	5227/31/533	5348/0/316
S on F^2	0.970	0.953	1.047	0.972	1.033
final R indices[a]					
[$I > 2\sigma(I)$]	$R_1 = 0.0744$, $wR_2 = 0.1486$	$R_1 = 0.0529$, $wR_2 = 0.1077$	$R_1 = 0.0691$ $wR_2 = 0.1651$	$R = 0.0714$, $wR = 0.1461$	$R_1 = 0.0436$ $wR_2 = 0.0918$
(all data)	$R_1 = 0.1681$, $wR_2 = 0.1843$	$R_1 = 0.1142$, $wR_2 = 0.1329$	$R_1 = 0.1179$ $wR_2 = 0.1829$	$R_1 = 0.1484$, $wR_2 = 0.1709$	$R_1 = 0.0723$ $wR_2 = 0.1079$
weights a, b[a]	0.0795, 0	0.0483, 0	0.0945, 0.6873	0.0760, 0	0.0438, 0.7628
max and min/e Å^{-3}	0.230/−0.333	0.260/−0.236	0.512/−0.518	0.316/−0.292	0.234/−0.245

[a] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^2$ where n = number of reflections and p = total number of parameters, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \sqrt{[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^2}$, $w^{-1} = [\Sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$.

ing non-hydrogen atoms were revealed from subsequent difference Fourier sytheses. A spherical region of residual electron density in **2** was intepreted as a totally disordered THF molecule in the lattice, and the individual maxima were included as partial atoms; this explained the rather poor diffraction by the crystals of **2**. In each of the structures **3d** and **3g** a molecule of benzene and in **3f** one toluene was located, and very high thermal displacement parameters for these atoms indicated some rotational disorder which was not resolved. Refinement was based on $F^{2,21}$ in the refinement of **2** and **3g** and chemically equivalent bond lengths within the tripod ligand were constrained to be equal within an esd of 0.02 Å. Because of the shortage of data, the phenylene rings in **2** were constrained to idealized hexagonal geometry (C−C 1.39 Å). All hydrogen atoms, apart from those of the severely disordered THF solvent molecule in **2**, were included in calculated positions with displacement parameters set equal to $1.2U_{eq}$ of the parent carbon atoms or $1.5U_{eq}$ for those of the methyl groups. After initial refinement with isotropic displacement parameters empirical absorption corrections[22] were applied to the data. All full-occupancy non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix least-squares refinement.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Engineering and Physical Sciences Research Council, the Fonds der Chemischen Industrie, the DAAD, and the British Council for financial support.

Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **2**, **3a**, **3d**, **3f**, **3g**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0005710

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