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New Titanium Imido Synthons: Syntheses and Supramolecular Structures

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Reactions of $Ti(NMe_2)_2Cl_2$ with a wide range of primary alkyl and arylamines RNH_2 afforded the corresponding 5-coordinate imido titanium compounds $Ti(NR)Cl_2(NHMe_2)_2$ (R = ^tBu (**1**), ^iPr (**2**), CH_2Ph (**3**), Ph (**4**), 2,6-$C_6H_3Me_2$ (**5**), 2,6-$C_6H_3{}^iPr_2$ (**6**), 2,4,6-$C_6H_2F_3$ (**7**), 2,3,5,6-C_6HF_4 (**8**), C_6F_5 (**9**), 4-C_6H_4Cl (**10**), 2,3,5,6-C_6HCl_4 (**11**), 2-$C_6H_4CF_3$ (**12**), 2-$C_6H_4{}^tBu$ (**13**)). The compounds **1**–**13** are monomeric in solution but in the solid state form either N–H···Cl hydrogen bonded dimers or chains or perfluorophenyl π-stacked chains, depending on the imido R-group. The compound **13** was also prepared in a “one-pot” synthesis from RNH_2 and $Ti(NMe_2)_4$ and Me_3SiCl. Reaction of certain $Ti(NR)Cl_2(NHMe_2)_2$ compounds with an excess of pyridine afforded the corresponding bis- or tris-pyridine analogues $[Ti(NR)Cl_2(py)_x]_y$ ($x = 3$, $y = 1$; $x = y = 2$), and the structure of $Ti_2(NC_6F_5)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ shows π-stacking of perfluorophenyl rings. Reaction of $Ti(NMe_2)_2Cl_2$ with cross-linked aminomethyl polystyrene gave quantitative conversion to the corresponding solid-supported titanium imido complex. This paper represents the first detailed study of how supramolecular structures of imido compounds may be influenced by simple variation of the imido ligand N-substituent.

Introduction

Transition metal imido compounds have been a focus of sustained activity for the past 20−25 years in particular. A number of general reviews,[1−3] as well as some more specific ones,[4−15] have documented the progress and achievements within this area of chemistry. In our group we have been especially interested in developing titanium imido chemistry.[13−15] As part of this work, we reported the synthesis and structures of the imido tris(pyridine) compounds $Ti(NR)Cl_2(py)_3$ (R = ^tBu or aryl).[16] These compounds have been remarkably successful as synthons, allowing access to many different types of new titanium imido complexes by chloride or/and pyridine ligand metathesis. The origins of our own work go back to Nielson’s[17] and then Winter’s[18,19] original investigations of the reactions of $TiCl_4$ with primary amines and subsequent reactions with Lewis bases.

However, while the syntheses of certain $Ti(NR)Cl_2(py)_3$ compounds have been optimized, these compounds are not without certain limitations. Only alkylimido derivatives (and in particular *tert*-butyl systems) can be directly accessed by the reaction of an excess of RNH_2 with $TiCl_4$ followed by

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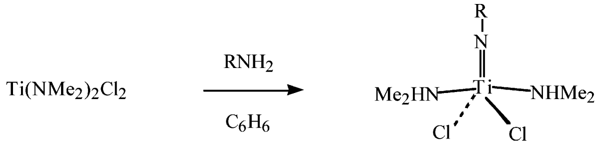
Scheme 1



R = ^{t}Bu (**1**), ^{i}Pr (**2**), CH_2Ph (**3**), Ph (**4**), 2,6-$C_6H_3Me_2$ (**5**), 2,6-$C_6H_3{}^iPr_2$ (**6**), 2,4,6-$C_6H_2F_3$ (**7**), 2,3,5,6-C_6HF_4 (**8**), C_6F_5 (**9**), 4-C_6H_4Cl (**10**), 2,3,5,6-C_6HCl_4 (**11**), 2-$C_6H_4CF_3$ (**12**), 2-$C_6H_4{}^tBu$ (**13**)

addition of an excess of pyridine. Use of anilines gives mixtures of products from which the anilinium salt side-products RNH_3Cl cannot be separated.[16] Arylimido compounds $Ti(NAr)Cl_2(py)_3$ are accessible by an aniline/*tert*-butyl imide exchange protocol, but with the exception of *ortho*-substituted anilines the products can be somewhat insoluble and rather capricious with regard to their workup. There can also be a tendency for residual $^tBuNH_2$ to remain associated with the desired $Ti(NAr)Cl_2(py)_3$ products, which sometimes forces the need for an additional treatment with pyridine and recrystallization. Finally, one of the pyridine ligands in $Ti(NR)Cl_2(py)_3$ is rather labile (due to the strong trans influence of imido ligands) and can be lost under dynamic vacuum giving dimeric, bis(imido) μ-chloride bridged products $Ti_2(NR)_2Cl_2(\mu\text{-}Cl)_2(py)_4$.[16,20,21]

As part of their pioneering work in transition metal amido chemistry, Bradley et al. reported that the reaction of $Ti(NMe_2)_4$ with $^tBuNH_2$ affords the μ-imido bridged dimers $Ti_2(\mu\text{-}N^tBu)_2(NMe_2)_4$ and $Ti_2(\mu\text{-}N^tBu)_2(NMe_2)_2(NH^tBu)_2$.[22] In a related reaction, we recently found[23] that monomeric terminal imido ansa-linked macrocycle complexes could be prepared by reaction of certain 1-aminopropyl-4,7-dialkyltriazacyclononanes with the dichloride-bis(amide) compound $Ti(NMe_2)_2Cl_2$. The compound $Ti(NMe_2)_2Cl_2$ is easily prepared[24] on a multigram scale by the redistribution reaction between $TiCl_4$ and $Ti(NMe_2)_4$, both of which are commercially available ($Ti(NMe_2)_4$ is also readily prepared from $TiCl_4$ and $LiNMe_2$[25,30]). The ready availability of $Ti(NMe_2)_2Cl_2$ and its potential use as a precursor to new titanium imido synthons prompted us to study the reactions between it and primary amines RNH_2 (R = alkyl, aryl) in general. Our preliminary results in this area have recently been communicated,[26] and a complete study of the synthesis and structures of compounds of the type $Ti(NR)Cl_2(NHMe_2)_2$ is the main topic of our present contribution. Very recently published work has firmly demonstrated the potential of compounds of the type $Ti(NR)Cl_2(NHMe_2)_2$ in the metal–organic chemical vapor deposition (MOCVD) synthesis of TiN thin films[27] and the synthesis of calix[4]arene-supported imido complexes,[28] as well as a 47-member library of titanium imido-based olefin polymerization catalysts (the compounds $Ti(NR)Cl_2(NHMe_2)_2$ were generated and reacted on in situ in this particular study).[29]

Results and Discussion

Synthesis of a Family of Compounds of the Type $Ti(NR)Cl_2(NHMe_2)_2$. The reaction between a dark red solution of $Ti(NMe_2)_2Cl_2$ and $^tBuNH_2$ in benzene gave a rapid color change to bright yellow. Subsequent evaporation of the volatiles allowed the isolation of the target compound $Ti(N^tBu)Cl_2(NHMe_2)_2$ (**1**) in 84% yield. When the reaction was repeated on an NMR tube scale (benzene-d_6), the ^1H NMR spectrum showed quantitative conversion to **1** with no side-products. This general protocol was readily extended to a range of other alkyl and arylamines affording the compounds listed in Scheme 1 as orange or yellow, air- and moisture-sensitive solids in 62–98% isolated yields. Full details of the characterizing data are provided in the Experimental Section, and detailed experimental procedures are provided in the Supporting Information.

The NMR spectra of the 13 new compounds $Ti(NR)Cl_2(NHMe_2)_2$ are all consistent with the structures proposed in Scheme 1, the spectra showing resonances for imido R groups and coordinated $NHMe_2$ ligands (the N*H* atoms appearing as a broad binomial septet and the N*Me*$_2$ hydrogens as a doublet in the ^1H spectra). There is no evidence that prolonged drying under dynamic vacuum at room temperature leads to loss of $NHMe_2$. Bearing in mind that 6-coordinate chloride-bridged dimers (at least in the solid state) have been found for a number of compounds of the type $Ti(NR)Cl_2(L)_2$, namely, $Ti_2(NR)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (R = ^{t}Bu, 2-C_6H_4Me, 2-$C_6H_4{}^tBu$, 2-C_6H_4Ph),[20,21] $Ti_2(N\text{-}2\text{-}C_6H_4\text{-}Ph)_2Cl_2(\mu\text{-}Cl)_2(TMEDA)_2$,[20] $Ti_2(N^tBu)_2Cl_2(\mu\text{-}Cl)_2(^tBuNH_2)_4$,[20] and $Ti_2(N^tBu)_2Cl_2(\mu\text{-}Cl)_2(MeCN)_2(^tBuNH_2)_2$,[31] we were careful to confirm the monomeric, 5-coordinate nature of six of the new compounds by X-ray crystallography as described in detail below. A cryoscopic solution molecular weight measurement of $Ti(N^iPr)Cl_2(NHMe_2)_2$ (**2**) in benzene gave a value of 291 g·mol^{-1} in reasonable agreement with the

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Table 1. Selected IR Data for the Compounds $Ti(NR)Cl_2(NHMe_2)_2$

compound (NR group)	ν(N−H) Nujol[a] (cm^{-1})	ν(N−H) CH_2Cl_2[b] (cm^{-1})
1 (R = ^{t}Bu)	3231	*c*
2 (R = ^{i}Pr)	3228	3288
3 (R = CH_2Ph)	3220	*c*
4 (R = Ph)	3220	3284
5 (R = 2,6-$C_6H_3Me_2$)	3242	*c*
6 (R = 2,6-$C_6H_3{}^iPr_2$)	3244	*c*
7 (R = 2,4,6-$C_6H_2F_3$)	3244	3282
8 (R = 2,3,5,6-C_6HF_4)	3258	3282
9 (R = C_6F_5)	3275	3280
10 (R = 4-C_6H_4Cl)	3228	*c*
11 (R = 2,3,5,6-C_6HCl_4)	3239	3280
12 (R = 2-$C_6H_4CF_3$)	3264	3284
13 (R = 2-$C_6H_4{}^tBu$).	3273[d]	3285
14 (R = $PSCH_2$)	3268	

[a] Nujol mull between KBr or NaCl plates. [b] CH_2Cl_2 solution, 0.1 mm path length NaCl cell. [c] Not recorded. [d] Partially resolved shoulder at 3258 cm^{-1}.

calculated value of 266.1 g·mol^{-1} for monomeric **2** (compound **2** is also monomeric in the solid state, vide infra). The compounds **1**−**13** all feature ν(N−H) bands in their IR spectra; these data are summarized in Table 1. In CH_2Cl_2 solution the values fall in the narrow range 3280−3288 cm^{-1} (8 compounds), but in the solid state the values span a much wider range (3220−3273 cm^{-1}). These data can be interpreted as reflecting the rather different N−H···Cl hydrogen bonded solid state structures formed (vide infra) whereas in solution the compounds are discretely monomeric.

The new compounds **1**−**13** are analogues of Lorber et al.'s vanadium(IV) complexes $V(NAr)Cl_2(NHMe_2)_2$ (Ar = Ph, C_6F_5, 2,6-$C_6H_3R_2$ (R = Me, ^{i}Pr, Cl)),[32] prepared via "one-pot" syntheses from $V(NMe_2)_4$, $ArNH_2$, and Me_3SiCl. We were interested to see if the titanium compounds could also be prepared via a one-pot route[33] and found that Ti(N-2-$C_6H_4{}^tBu$)$Cl_2(NHMe_2)_2$ (**13**) could indeed be made directly from $Ti(NMe_2)_4$, H_2N-2-$C_6H_4{}^tBu$, and Me_3SiCl in toluene at 80 °C (72% yield, cf. 74% for the route starting from $Ti(NMe_2)_2Cl_2$ and H_2N-2-$C_6H_4{}^tBu$).

Structural Studies of the Compounds $Ti(NR)Cl_2(NHMe_2)_2$. The X-ray crystal structures for the six compounds $Ti(NR)Cl_2(NHMe_2)_2$ (R = ^{i}Pr (**2**), Ph (**4**), C_6F_5 (**9**), 2,3,5,6-C_6HCl_4 (**11**), 2-$C_6H_4CF_3$ (**12**), or 2-$C_6H_4{}^tBu$ (**13**)) have been determined. Key bond distances and angles are compared in Table 2, and views of the molecular structures are collected together in Figure 1 (**2**, **4**, **9**, and **11**) and Figure 2 (**12** and **13**). Details of the structure determinations are given in the Experimental Section and Table 3 and will not be further discussed. However, it should be noted that for the purposes of discussion of the N−H···Cl bonding (vide infra), we refer in all instances to geometrically positioned (N−H = 0.87 Å, sp^3 hybridized N) N*H*Me_2 hydrogens (regardless of whether the N*H*Me_2 hydrogens for a particular structure were found or not from Fourier difference maps).

All six compounds exist as monomeric, 5-coordinate complexes in the solid state. Crystals of **2**, **4**, and **9** feature the same space group (*C*2/*c*) with the $Ti{=}N_{im}$ vectors lying on crystallographic 2-fold rotation axes at (0, *y*, $^1/_4$) or a symmetry equivalent position; other molecules lie on general positions, and crystals of **11** and **13** contain residual solvent (benzene and pentane, respectively) of crystallization. The geometries at titanium are approximately trigonal bipyramidal ($NHMe_2$ groups axial) with $N_{im}{=}Ti{-}Cl$ angles in the range 108.62(2)−114.79(1)° (avg 111.3°) and $N_{im}{=}Ti{-}N_{am}$ angles in the range 95.34(3)−101.58(6)° (avg 98.3°). Only one 5-coordinate titanium imido dichloride compound with monodentate Lewis base ligands is recorded in the Cambridge Structural Database,[34,35] namely Ti(N^{t}Bu)$Cl_2(OPPh_3)_2$,[18,19] and this appears to have a similar geometry (avg $N_{im}{=}Ti{-}Cl$ = 108.1°, avg $N_{im}{=}Ti{-}O$ = 102.7°) to those reported here. Solid state structures of three other monomeric, 5-coordinate titanium imido dichloride com-

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Ti(NR)Cl_2(NHMe_2)_2$ (R = ^{i}Pr (**2**), Ph (**4**), C_6F_5 (**9**), 2,3,5,6-C_6HCl_4 (**11**), 2-$C_6H_4CF_3$ (**12**), or 2-$C_6H_4{}^tBu$ (**13**))[a]

	2	**4**	**9**	**11**	**12**	**13**
			Distances			
$Ti{=}N_{im}$	1.672(2)	1.7024(14)	1.706(3)	1.7079(18)	1.705(4) [1.694(4)]	1.7023(17)
$Ti{-}Cl$	2.3544(5)	2.3406(3)	2.3373(7)	2.3293(6) 2.3319(6)	2.3397(16) [2.3440(16)] 2.3486(18) [2.3401(18)]	2.3209(6) 2.3638(7)
$Ti{-}N_{am}$	2.2067(17)	2.201(1)	2.201(2)	2.1894(18) 2.1992(18)	2.205(5) [2.202(6)] 2.199(4) [2.197(4)]	2.206(2) 2.2126(19)
$N_{im}{-}C$	1.476(5)	1.380(2)	1.359(5)	1.367(3)	1.378(6) [1.385(5)]	1.395(3)
$N_{am}H{\cdots}Cl$	2.53	2.45	2.95	2.59 2.74	2.67 [2.68] 2.78 [2.81]	2.64
			Angles			
$N_{im}{=}Ti{-}N_{am}$	97.72(5)	95.34(3)	101.58(6)	100.00(8) 97.10(8)	100.1(2) [100.1(2)] 97.4(2) [97.67(19)]	98.07(8) 96.52(8)
$N_{im}{=}Ti{-}Cl$	112.655(19)	114.79(1)	108.62(2)	110.54(7) 110.92(7)	109.53(14) [109.37(14)] 110.90(14) [110.80(14)]	110.49(6) 113.07(6)
$Cl{-}Ti{-}Cl$	134.69(4)	130.42(2)	142.75(5)	138.51(3)	139.56(11) [139.82(11)]	136.41(3)
$N_{am}{-}Ti{-}N_{am}$	164.56(9)	169.32(6)	156.83(13)	162.89(7)	162.4(3) [162.2(2)]	165.14(7)
$Ti{=}N_{im}{-}C$	164.46(17)	180	180	173.11(16)	175.7(3) [175.6(3)]	165.84(16)
$N_{am}{-}H{\cdots}Cl$	160	161	148	152.8 149.3	140 [139] 137 [134]	150

[a] Parameters involving N−H···Cl interactions are calculated assuming N−H = 0.87 Å and an sp^3 hybridized N_{am}. Values in brackets for **12** correspond to the other crystallographically independent molecule in the asymmetric unit. Molecules of **2**, **4**, and **9** lie on crystallographic C_2 rotation axes and only have only one crystallographically independent Ti−Cl and $Ti{-}N_{am}$ unit. Molecules of **13** lie across crystallographic inversion centers. N_{am} and N_{im} refer to the amino ($NHMe_2$) and imido (Ti═NR) nitrogens, respectively.

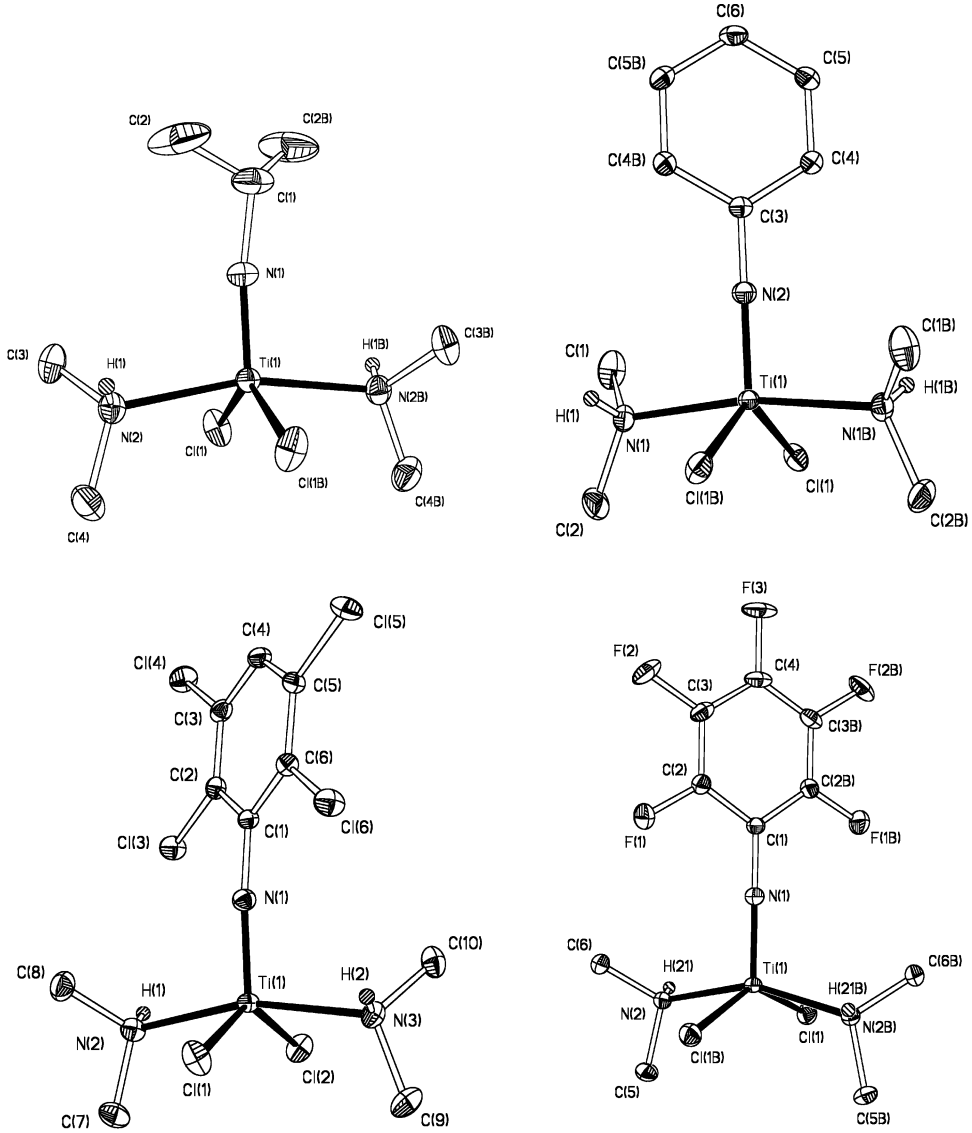

Figure 1. Displacement ellipsoid plots of $Ti(N^{i}Pr)Cl_2(NHMe_2)_2$ (**2**, 25% probability, top left), $Ti(NPh)Cl_2(NHMe_2)_2$ (**4**, 25% probability, top right), $Ti(NC_6F_5)Cl_2(NHMe_2)_2$ (**9**, 25% probability, bottom left), and $Ti(N\text{-}2,3,5,6\text{-}C_6HCl_4)Cl_2(NHMe_2)_2$ (**11**, 35% probability, bottom right). Solvent of crystallization and H atoms bound to C are omitted. N−*H* atoms are drawn as spheres of arbitrary radius.

pounds are known,[20,36] but these have cis-chelating TMEDA Lewis bases and the geometries are better described as square base pyramidal. Five 5-coordinate structures of the type $Ti(NR)(OR')_2(L)_2$ (R = ^{t}Bu, aryl; R′ = aryl, $BMes_2$, or $CH(Mes)_2$; L = py or $4\text{-}NC_5H_4NC_4H_8$) have been reported, and in all these cases the metal center also has a trigonal bipyramidal geometry.[37−40] Lorber et al.'s $V(NAr)Cl_2(NHMe_2)_2$ complexes also feature trigonal bipyramidal geometries in the solid state.[32]

In broad terms, the distances and angles associated with the titanium centers and the ligands themselves are within known ranges.[34,35] In terms of specific comparisons with the 6-coordinate complexes $Ti(NR)Cl_2(py)_3$[16] (R = ^{t}Bu, Ph, $4\text{-}C_6H_4Me$, $4\text{-}C_6H_4NO_2$), the $Ti{=}N_{im}$ and Ti−Cl distances for $Ti(NR)Cl_2(NHMe_2)_2$ are somewhat shorter, presumably reflecting both the decreased coordination number in the latter cases and the better σ-donor Lewis bases in the tris(pyridine) systems. The $Ti{=}N_{im}$ distance is shorter and the Ti−Cl longer for the alkylimido compound **2** compared to the other five (arylimido) compounds. This mirrors trends established in the 6-coordinate complexes $Ti(NR)Cl_2(py)_3$[16] and in alkyl- and aryl-imido compounds in general.[34,35] There

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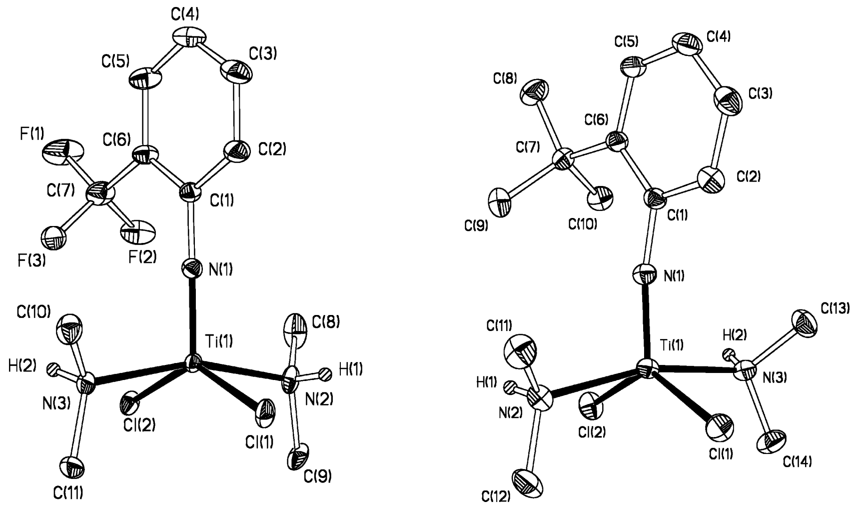

Figure 2. Displacement ellipsoid plots of one of the two crystallographically independent molecules of Ti(N-2-$C_6H_4CF_3$)Cl_2($NHMe_2$)$_2$ (**12**, 30% probability, left) and Ti(N-2-$C_6H_4{}^tBu$)Cl_2($NHMe_2$)$_2$ (**13**, 30% probability, right). Solvent of crystallization and H atoms bound to C are omitted. N−*H* atoms are drawn as spheres of arbitrary radius. A view of the other crystallographically independent molecule of **12** is provided in the Supporting Information (Figure S7).

Table 3. X-ray Data Collection and Processing Parameters for Ti(NR)Cl_2($NHMe_2$)$_2$ (R = ^{i}Pr (**2**), Ph (**4**), C_6F_5 (**9**), 2-$C_6H_4CF_3$ (**12**)), Ti(N-2,3,5,6-C_6HCl_4)Cl_2($NHMe_2$)$_2$·0.5(C_6H_6) (**11·0.5(C_6H_6)**), Ti(N-2-$C_6H_4{}^tBu$)Cl_2($NHMe_2$)$_2$·0.5(C_5H_{12}) (**13·0.5(C_5H_{12})**), and Ti_2(NC_6F_5)$_2Cl_2$(μ-Cl)$_2$(py)$_4$ (**17**)

	2	**4**	**9**	**11·0.5(C_6H_6)**	**12**	**13·0.5(C_5H_{12})**	**17**
empirical formula	$C_7H_{21}Cl_2N_3Ti$	$C_{10}H_{19}Cl_2N_3Ti$	$C_{10}H_{14}Cl_2F_5N_3Ti$	$C_{10}H_{15}Cl_6N_3Ti$· 0.5C_6H_6	$C_{11}H_{18}Cl_2F_3N_3Ti$	$C_{14}H_{27}Cl_2N_3Ti$· 0.5C_5H_{12}	$C_{32}H_{20}Cl_4F_{10}N_6Ti_2$
fw	266.07	300.08	390.04	476.92	368.08	392.27	916.14
temp/K	175 K	150	200	150	150	150	150
wavelength/Å	0.71073	0.71073	1.54180	0.71073	0.71073	0.71073	0.71073
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	$P\bar{1}$	*Pna*2$_1$	*P*2$_1$/*n*	*P*2$_1$/*n*
a/Å	16.913(1)	16.260(1)	15.696(3)	7.3945(1)	16.1331(2)	10.5572(2)	7.2324(2)
b/Å	9.101(1)	10.303(1)	15.569(1)	12.7544(2)	6.5142(2)	11.4410(3)	18.1474(5)
c/Å	12.044(1)	11.935(1)	6.7371(9)	12.9622(2)	32.3906(5)	18.3161(5)	13.7813(3)
α/deg	90	90	90	115.6105(9)	90	90	90
β/deg	128.78(5)	131.01(1)	109.69(2)	90.7721(8)	90	96.8053(10)	103.425(1)
γ/deg	90	90	90	106.112(1)	90	90	90
V/Å^3	1445.1	1508.8	1550.1	1046.45	3404.07	2196.72	1759.4
Z	4	4	4	2	8	4	2
d (calcd)/Mg·m^{-3}	1.22	1.321	1.671	1.513	1.436	1.186	1.73
abs coeff/mm^{-1}	0.930	0.902	8.334	1.175	0.838	0.635	0.84
R indices R_1, R_w [$I > 3\sigma(I)$]^a	$R_1 = 0.0271$, $R_w = 0.0326$	0.0250, 0.0307	0.0615, 0.0648	0.0341, 0.0408	0.0364, 0.0343	0.0324, 0.0357	0.0294, 0.0407

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2\}}$.

are few other features of distinction associated with the molecular structures of individual compounds (the different relative orientation of the $NHMe_2$ ligands in **13** will be discussed below), and it is not clear to what extent some of the more subtle differences between individual molecular structures could be attributable to crystal packing effects and the various supramolecular interactions which we shall now discuss.

With the exception of Ti(NC_6F_5)Cl_2($NHMe_2$)$_2$ (**9**), the supramolecular structures of all of the structurally characterized compounds are dominated by Me_2N−H···Cl hydrogen bonding between the 5-coordinate complexes. Hydrogen bonds in general[41] have been described as "the most important of all intermolecular interactions".[42] Of particular relevance to this work are hydrogen bonds donated by N−H to metal-bound chloride. These are well-established[43] and have been categorized as "short" (intermolecular contact ≤ 2.52 Å), "intermediate" (2.52−2.95 Å), and "long" (2.95−3.15 Å; *NB*, the sum of the van der Waals radii for H and Cl, is 2.95 Å[44]).

Figures 3−5 illustrate the extended packing in the compounds Ti(NR)Cl_2($NHMe_2$)$_2$ for R = Ph (**4**), 2,3,5,6-C_6HCl_4 (**11**), and 2-$C_6H_4CF_3$ (**12**), respectively, with each molecule donating two N−H···Cl hydrogen bonds and accepting two, and each Ti being a common member of two eight-membered rings. The supramolecular arrangement of the isopropylimido compound Ti(N^{i}Pr)Cl_2($NHMe_2$)$_2$ (**2**) is similar to that of **4**, and a partial packing diagram is given in the Supporting Information (Figure S1). Both **2** and **4** crystallize in the *C*2/*c* space group with metals lying on crystallographic 2-fold axes (passing through the Ti=N_{im} bonds parallel with the *b* axis) at (0, *y*, $^1/_4$). The infinite N−H···Cl hydrogen bonded chains propagate along the

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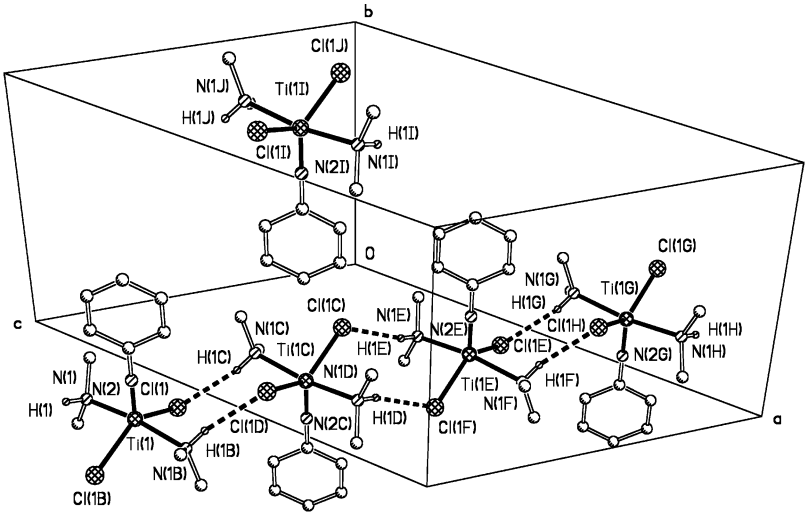

Figure 3. Partial packing diagram for $Ti(NPh)Cl_2(NHMe_2)_2$ (**4**) showing a portion of the infinite N−H···Cl hydrogen bonded chains. H atoms bound to C are omitted, and all atoms are drawn as spheres of arbitrary radius. Symmetry operators: B, [$3-x$, y, $-z+{}^5/_2$]; C, [x, $-y$, $z-{}^1/_2$]; D, [$3-x$, $-y$, $-z+2$]; E, [x, y, $z-1$]; F, [$3-x$, y, $-z+{}^3/_2$]; G, [x, $-y$, $z-{}^3/_2$]; H, [$3-x$, $-y$, $-z+1$]; I, [$3-x$, $1-y$, $2-z$]; J, [x, $1-y$, $z-{}^1/_2$].

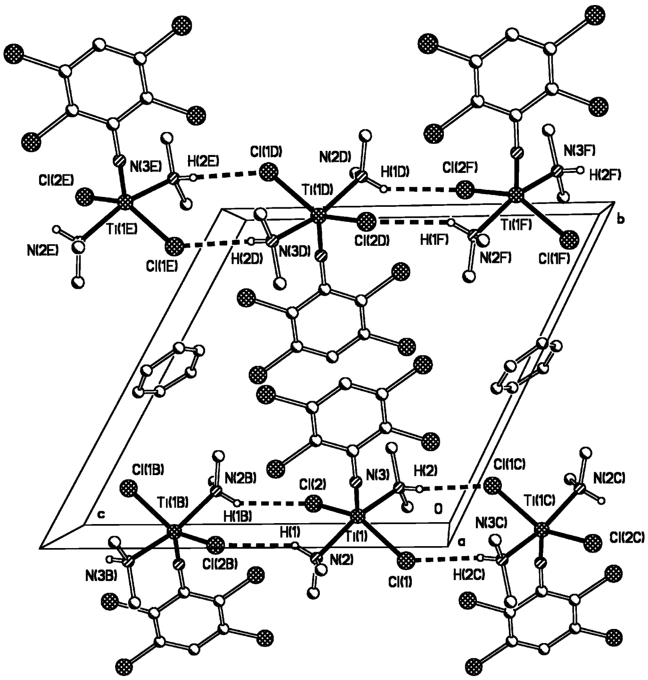

Figure 4. Cell packing diagram for $Ti(N\text{-}2,3,5,6\text{-}C_6HCl_4)Cl_2(NHMe_2)_2\cdot 0.5(C_6H_6)$ (**11·0.5C₆H₆**) showing a portion of the infinite N−H···Cl hydrogen bonded chains. H atoms bound to C are omitted, and all atoms are drawn as spheres of arbitrary radius. Symmetry operators: B, [$-x$, $-y$, $1-z$]; C, [$-x$, $-y$, $-z$]; D, [$1-x$, $1-y$, $1-z$]; E, [$1+x$, $1-y$, $1-z$]; F, [$1+x$, $1+y$, $1+z$].

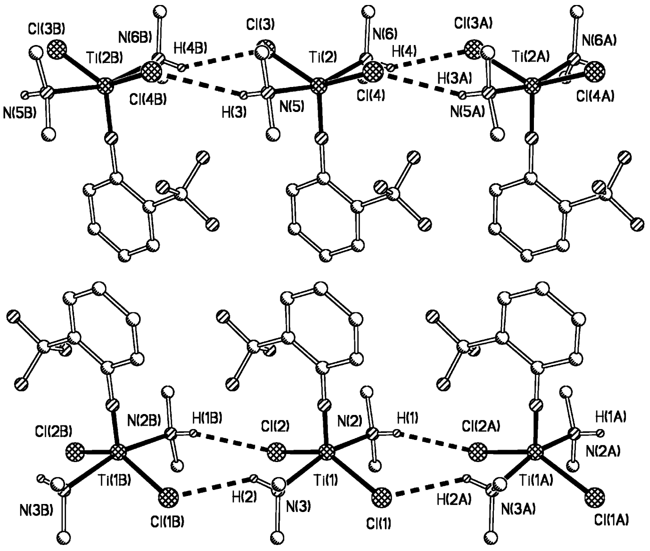

Figure 5. Extended packing diagram for $Ti(N\text{-}2\text{-}C_6H_4CF_3)Cl_2(NHMe_2)_2$ (**12**) showing a portion of the infinite N−H···Cl hydrogen bonded bilayers. H atoms bound to C are omitted, and all atoms are drawn as spheres of arbitrary radius. Symmetry operators: B, [x, $y+1$, z]; C, [x, $y-1$, z].

crystallographic *c* axis, and the NH···Cl contacts (2.53 and 2.45 Å) can be classified as "short". In this context we note that the solid state ν(N−H) bands for **2** and **4** (3228 and 3220 cm^{-1}, respectively) are among the lowest energy stretches for the 14 compounds listed in Table 1, presumably reflecting the strong N−H···Cl hydrogen bonding. There are no close contacts between the phenyl rings in **4** (the closest intermolecular C···C distance is 3.803(2) Å; the closest C−H···C inter-ring contact is 3.08 Å; see Figure S2 in the Supporting Information).

Crystals of $Ti(N\text{-}2,3,5,6\text{-}C_6HCl_4)Cl_2(NHMe_2)_2$ (**11**, Figure 4) contain benzene molecules of crystallization which are disordered across crystallographic inversion centers but exhibit no close contacts to the metal complexes. Molecules of **11** also form infinite N−H···Cl hydrogen bonded chains in which the $Ti{=}N_{im}$ bonds alternate "up and down" along the chains just as for **2** and **4**. The NH···Cl distances are "intermediate" (avg 2.67 Å), and the solid state ν(N−H) band appears at 3239 cm^{-1}. The CH_2Cl_2 solution ν(N−H) values for **11** (3280 cm^{-1}) and **4** (3284 cm^{-1}) differ by only $\Delta\nu = 4$ cm^{-1}. This is consistent with the differences between the two values in the solid state ($\Delta\nu = 19$ cm^{-1}) being attributable to differing extents of N−H···Cl hydrogen bonding.

Although the arrangement of Ti═NR units (alternating "up and down") *within* the infinite chains is comparable for **4** and **11**, there is a difference in the extent of $\pi-\pi$ interaction between the imido aryl groups *between* the chains as indicated in Figure 4 (see also Figure S3 in the Supporting Information). The N-bound C_6HCl_4 rings of Ti(1) and Ti(1D) are arranged in a favorable[45−47] offset face to face (*off*) arrangement of $\pi-\pi$ interactions. The closest inter-ring C···C contact is 3.436(3) Å, and the average interplanar spacing is 3.44 Å. It appears that the presence of the four electron-withdrawing Cl substituents on the arene rings is responsible for the additional supramolecular interactions in **11**. Accommodating these additional interactions might be correlated with the slight disruption to the NH···Cl hydrogen bond contacts.

Crystals of $Ti(N\text{-}2\text{-}C_6H_4CF_3)Cl_2(NHMe_2)_2$ (**12**, Figure 5) again feature N−H···Cl hydrogen bonded chains, but the detailed arrangements differ from the three systems discussed so far. Whereas the chains of **2**, **4**, and **11** have alternating "up and down" Ti═NR units (with additional *off* $\pi-\pi$ interactions between the chains for **11**), the $Ti{=}N\text{-}2\text{-}C_6H_4\text{-}CF_3$ units in **12** are all oriented on the same side of the infinite chains. The chains themselves are arranged in a pairwise fashion by noncrystallographic inversion centers which relate the two molecules in each asymmetric unit (Ti(1) and Ti(2) in Figure 5). The NH···Cl distances are again "intermediate" (avg 2.73 Å, consistent with the solid state IR data (Table 1)), but unlike **11** (where longer hydrogen bonds are accompanied by additional $\pi-\pi$ interactions) the closest C···C contact between the neighboring $C_6H_4CF_3$ rings is 3.872(6) Å and the separation between the C(1)−C(6) and C(12)−C(17) least-squares planes is 3.85 Å (see Figure S4 in the Supporting Information). There are no other significant close contacts.

Crystals of $Ti(NC_6F_5)Cl_2(NHMe_2)_2$ (**9**, Figure 6) possess "long" (possibly negligible) N−H···Cl hydrogen bonds (NH···Cl = 2.95 Å which is the sum of the van der Waals radii for H and Cl[44]). The disruption to the hydrogen bonding is reflected in the higher solid state ν(N−H) value (3275 cm^{-1}, Table 1). However, the hydrogen bonding is replaced by well-defined $\pi-\pi$ stacking of C_6F_5 rings arranged in an offset face-to-face manner propagating along the crystallographic *c* axis (see also Figure S5 in the Supporting Information). The closest C···F and C···C intermolecular contacts are 3.256(4) and 3.264(3) Å, respectively, and the separation between C_6F_5 computed least-squares planes is 3.23 Å. Intermolecular $\pi-\pi$ interactions between perfluorophenyl rings have recently received increased attention both computationally and experimentally,[47−52] and the intermolecular contacts found in **9** are comparable to the closest contacts reported to date. It has been proposed that intermolecular interactions between perfluorinated aromatic rings are slightly *more* attractive than the very well-established ones between their hydro analogues (due mainly to an increased van der Waals component).[47] The structures of $Ti(NPh)Cl_2(NHMe_2)_2$ (**4**) and $Ti(NC_6F_5)Cl_2(NHMe_2)_2$ (**9**) appear to support this.

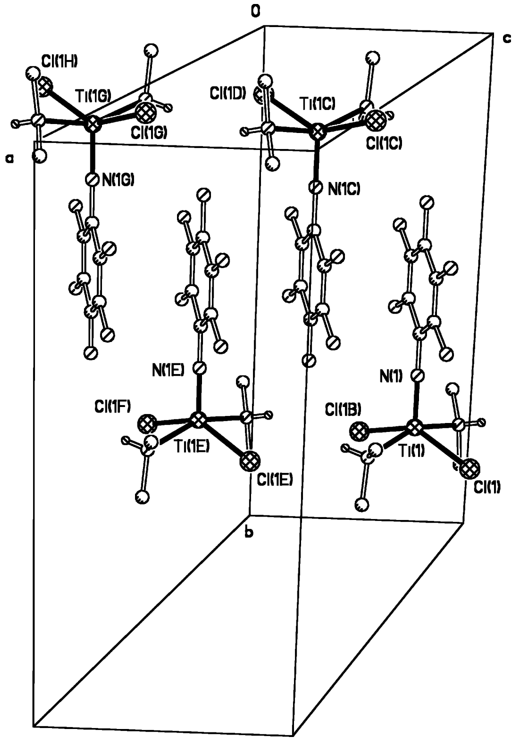

Figure 6. Partial cell packing diagram for $Ti(NC_6F_5)Cl_2(NHMe_2)_2$ (**9**) showing a portion of the infinite π-stacked chains. H atoms bound to C are omitted, and all atoms are drawn as spheres of arbitrary radius. Symmetry operators: B, [$-x, y, -z+{}^3/_2$]; C, [$x, -y-1, z-{}^1/_2$]; D, [$-x, -y-1, -z+1$]; E, [$x, y, z-1$]; F, [$-x, y, -z+{}^1/_2$]; G, [$x, -y-1, z-{}^3/_2$], H [$-x, -y-1, -z$].

It is also interesting to compare the solid state and solution ν(N−H) data (Table 1) for the series of compounds $Ti(NAr)Cl_2(NHMe_2)_2$ (Ar = Ph (**4**), 2,4,6-$C_6H_2F_3$ (**7**), 2,3,5,6-C_6HF_4 (**8**), and C_6F_5 (**9**)). The solid state ν(N−H) increases by 55 cm^{-1} with increasing fluorination of the phenyl ring (3220 cm^{-1} for Ar = Ph to 3275 cm^{-1} for Ar = C_6F_5), whereas there is only a small change in the solution phase ν(N−H) (3284 cm^{-1} for Ar = Ph to 3280 cm^{-1} for Ar = C_6F_5) and in the opposite sense (i.e., a *lower* value for Ar = C_6F_5). Although we were unable to obtain diffraction-quality crystals of either **7** or **8**, the IR data might be reflecting an increased tendency for $\pi-\pi$ stacking with increased fluorination of the phenyl ring. We note also that the solid state ν(N−H) data reported by Lorber et al. for $V(NAr)Cl_2(NHMe_2)_2$ are 3232 and 3252 cm^{-1} for Ar = Ph and C_6F_5, respectively.[32] Neither of these compounds was crystallographically characterized, but the difference of 20 cm^{-1} between the two ν(N−H) bands is consistent with a decrease in NH···Cl−V hydrogen bonding in the perfluorophenyl imido complex.

The supramolecular structure of $Ti(N\text{-}2\text{-}C_6H_4{}^tBu)Cl_2(NHMe_2)_2$ (**13**, Figure 7) is again different from those already discussed. Molecules of **13** form only hydrogen bonded dimers across crystallographic inversion centers. Only one $NHMe_2$ hydrogen per metal center is involved in a significant N−H···Cl hydrogen bond (H(1)···Cl(2A) = 2.64 Å); the

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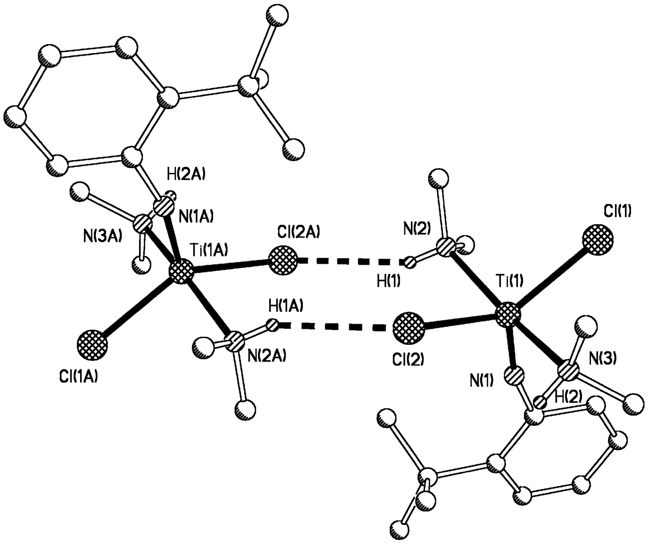
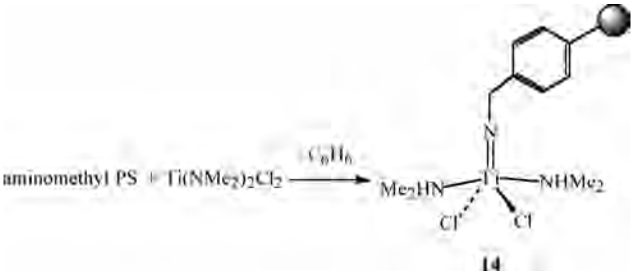


Figure 7. View of the N−H···Cl hydrogen bonded dimer formed by molecules of Ti(N-2-$C_6H_4{}^tBu$)Cl_2($NHMe_2$)$_2$ (**13**) in the solid state. H atoms bound to C are omitted, and all atoms are drawn as spheres of arbitrary radius. Atoms carrying the suffix A are related to their counterparts by the symmetry operator [$-x$, $1-y$, $-z$].

other (H(2)) is not. The solid state IR spectrum is consistent with the X-ray structure and possesses two overlapping ν(N−H) bands at 3273 cm^{-1} (assigned to the nonbridging N−H bond) and 3258 cm^{-1} (attributed to the hydrogen bonded N−H). In dichloromethane solution, a single ν(N−H) of 3285 cm^{-1} is observed. The unexpected supramolecular arrangement of **13** is reflected in the molecular structure (Figure 2 compares the molecular structures of the *ortho*-CF_3 homologue **12** and that of **13**). In **12** (and in *all* the other structurally characterized compounds, Figure 1) the Me_2N_{am}−H bonds are oriented in a trans orientation across the N_{am}−Ti−N_{am} unit, whereas in **13** the N−H bonds are in a cis conformation. In other words the N−H bonds are orientated in the *same* direction in **13** and in *opposite* directions for the other five compounds. The cis arrangement of N−H bonds in **13** removes the possibility of forming analogous extended hydrogen bonded chains and appears to lead to the dimeric structure shown in Figure 7. A N−H···Cl hydrogen bonded imido vanadium dimer reminiscent of that found for **13** was reported recently (N−H···Cl = 2.31 Å).[53]

A closer examination of the molecular structure of **13** shows that the cis-orientated N−H bonds lie on the same side of the molecule as the bulky ortho *tert*-butyl group. We speculated that avoidance of intramolecular repulsions between the NH*Me*$_2$ methyl groups and the ortho *tert*-butyl group that might result from a *trans*-N−H conformation (cf. **12**) could be a reason for the different conformation found in **13** (Figure S6 of the Supporting Information shows space-filling models for **12** and **13**). To probe for intramolecular steric effects, molecular modeling studies were carried out on different possible conformations of **12** and **13** generated by rotations of the Ti−$NHMe_2$ bonds using the semiempirical method PM3 in SPARTAN ’04 (Wavefunction, Inc.). Metal−ligand bond distances and ligand−metal−ligand angles were constrained to those values determined by single-crystal X-ray diffraction methods. For **13** the cis N−H bond orientation (N−H bonds on the same side as the *tert*-butyl group) was found to be 5.2 kcal·mol^{-1} *more* favorable than the alternative trans N−H bond orientation. For **12**, however, the cis N−H bond orientation was 3.4 kcal·mol^{-1} *less* stable than the alternative trans N−H bond orientation (the same side as the ortho CF_3 group). The conformers in which cis N−H bonds lie on the *opposite* side of the molecule from the ortho ^{t}Bu or CF_3 groups (i.e., conformations not observed in any of the crystal structures) were calculated to be 16.1 and 5.4 kcal·mol^{-1} higher in energy than the minimum energy conformations for **13** and **12**, respectively. These results suggest that the supramolecular structures of **12** and **13** are probably governed to some extent by quite subtle intramolecular repulsions.

Scheme 2



Further Studies. Solid phase supported reagents and catalysts are an important area of current interest.[54−57] Two reports of cross-linked polystyrene (PS) supported imido complexes have recently appeared in the context of olefin polymerization catalysis, these being CpV(N-4-C_6H_4PS)Cl_2,[58] Ti(N-4-C_6H_4PS)Cl_2(TMEDA), and Ti(N^tBu)Cl_2($Me_2NCH_2CH_2NMeCH_2$PS).[20] The first two of these compounds were prepared *indirectly* via an arylamine/*tert*-butyl imide exchange protocol ($^tBuNH_2$ elimination) between H_2N-4-C_6H_4-PS and either CpV(N^tBu)Cl_2 or Ti(N^tBu)Cl_2(TMEDA). We were interested to see if Ti(NMe_2)$_2Cl_2$ could act as a *direct* precursor to polystyrene-supported titanium imido complexes as this approach would offer considerable scope for the subsequent assembly of additional donor ligands around the already-supported metal center (in the same way that the solution phase compounds Ti(NR)Cl_2(L)$_n$ (L = py or $NHMe_2$, n = 2 or 3) allow access to a wide number of new titanium imido derivatives).

Shaking (to avoid mechanical damage by stirring) a pre-swollen (benzene) sample of 1% cross-linked commercially available aminomethyl polystyrene resin (H_2NCH_2-4-C_6H_4-PS; 1.19 mmol·g^{-1} loading) with Ti(NMe_2)$_2Cl_2$ (1 equiv) in benzene over 16 h gave quantitative uptake of the titanium to form dark red Ti(N−CH_2-4-C_6H_4PS)Cl_2($NHMe_2$)$_2$ (**14**) and a colorless supernatant (Scheme 2). The

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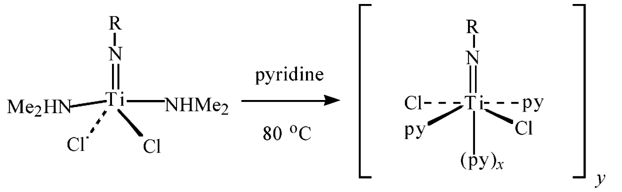
supernatant contained negligible $Ti(NMe_2)_2Cl_2$ as judged by ^1H NMR spectroscopy. The IR spectrum of **14** showed no ν(N−H) bands for the primary amino groups of the starting H_2NCH_2-4-C_6H_4PS resin, but a new band at 3268 cm^{-1} was evident. This is attributed to ν(N−H) of the new $NHMe_2$ ligands in **14** and may be contrasted with the value of 3220 cm^{-1} found in the solid state for $Ti(NCH_2Ph)Cl_2(NHMe_2)_2$ (**3**). The benzylimido compound **3** may be viewed as a simplified model for **14**. The substantially increased ν(N−H) found in **14** is attributed to decreased intermolecular N−H···Cl hydrogen bonding associated with the greater site isolation in the supported system. The 400 MHz ^1H gel-phase magic angle spinning (MAS) NMR spectrum of **14** showed a new resonance at 4.33 ppm attributed to $Ti{=}NCH_2$ (shifted from 3.70 in the starting H_2NCH_2-4-C_6H_4PS resin, this resonance being absent in the spectrum of **14**) and new resonances for the coordinated $NHMe_2$ ligands at 3.27 (N*H*Me_2) and 2.49 (NH*Me_2*) ppm. The ^{13}C-{^1H} spectrum was also consistent with the formation of **14**, notably featuring a distinctive resonance at 72.9 ppm for $Ti{=}NCH_2$. Regrettably, the elemental analysis of the product repeatedly returned lower than expected % N, Cl, Ti values. This is attributed to incomplete combustion or acid digestion, but we believe that the spectroscopic data and other experimental evidence discussed above provide firm evidence for the formation of **14**. Preliminary studies have shown that **14** is indeed a useful precursor to new polymer-supported imido complexes,[59] and we will report on this chemistry in a future contribution.

As mentioned, Cl or/and $NHMe_2$ ligand substitution of certain $Ti(NR)Cl_2(NHMe_2)_2$ complexes have allowed direct access to new classes of calix[4]arene[28] and triazacyclononane-supported imido complexes.[29] Nonetheless, it was also of interest to determine whether the new compounds would also allow access to new and/or previously reported tris- or bis(pyridine) compounds $[Ti(NR)Cl_2(py)_x]_y$ ($x = 3$, $y = 1$; $x = y = 2$) since in some of the new, reactive titanium imido compounds (e.g., $Cp_2Ti(NR)(py)$, $Ti(N_2N_{py})(NR)(py)$ (N_2N_{py} = MeC(2-C_5H_4N)(CH_2NSiMe_3)$_2$) pyridine is necessary for stabilizing the product.

Scheme 3



x = 1 or 0; y = 1 or 2; R = ^tBu, C_6F_5 or 4-C_6H_4Cl

Table 4. Selected Bond Lengths and Intermolecular Contacts (Å) and Angles (deg) for $Ti_2(NC_6F_5)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (**17**)[a]

Ti(1)−N(1)	1.720(3)	C(1)···F(4C)	3.317(4)
Ti(1)−Cl(1)	2.337(1)	C(4)···F(4E)	3.200(5)
Ti(1)−Cl(2)	2.445(1)	C(4)···F(5C)	3.303(5)
Ti(1)−Cl(2B)	2.705(1)	C(5)···C(6C)	3.341(5)
Ti(1)−N(2)	2.216(3)	C(5)···F(3E)	3.068(5)
Ti(1)−N(3)	2.212(3)		
Ti(1)−N(1)−C(1)	165.9(3)	N(1)−Ti(1)−N(2)	91.8(1)
Ti(1)−Cl(2)−Ti(1B)	101.50(3)	N(1)−Ti(1)−N(3)	95.9(1)
N(1)−Ti(1)−Cl(2)	100.2(1)	N(1)−Ti(1)−Cl(1)	98.1(1)
N(1)−Ti(1)−Cl(2B)	177.5(1)	N(2)−Ti(1)−N(3)	170.2(1)

[a] Atoms carrying the suffixes B, C, and E are related to their counterparts in the asymmetric unit by the operators [1−x, −y, 1−z], [1−x, −y, −z], and [2−x, −y, −z], respectively.

Preliminary NMR tube scale reactions of a number of the compounds $Ti(NR)Cl_2(NHMe_2)_2$ with 3−4 equiv of pyridine in benzene-d_6 gave rise to mixtures of products even where the target compounds themselves have been prepared previously (e.g., attempting to form $Ti(N^tBu)Cl_2(py)_3$ from $Ti(N^tBu)Cl_2(NHMe_2)_2$). It appears that $NHMe_2$ ligands can be competitive with pyridine under these conditions. Similar problems have been noted previously by Lorber et al. in the $NHMe_2$ substitution chemistry of $V(NAr)Cl_2(NHMe_2)_2$.[32] This problem can be circumvented to some extent by use of neat pyridine at 80 °C (Scheme 3) which affords the previously described[16,21] $Ti_2(N^tBu)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ and the new compounds $Ti(NC_6F_5)Cl_2(py)_3$ (**15**) and Ti(N-4-C_6H_4-Cl)$Cl_2(py)_3$ (**16**) in reasonable to excellent yields. The NMR and other data for **16** suggest that some loss of the *trans*-pyridine has occurred, and the isolation of $Ti_2(N^tBu)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (as opposed to the known[16] $Ti(N^tBu)Cl_2(py)_3$) is also consistent with the tendency of tris(pyridine) titanium imido compounds to lose the third pyridine ligand.[16,20] However, even use of neat pyridine at 80 °C does not allow the clean formation of certain $Ti(NR)Cl_2(py)_n$ compounds (for R = ^iPr, CH_2Ph, 2,6-$C_6H_3{}^iPr_2$), even though, for R = 2,6-$C_6H_3{}^iPr_2$, the target complexes may be prepared in pure form by an alternative route.[16] The reasons for these rather subtle differences differences between the various $Ti(NR)Cl_2(NHMe_2)_2$ systems are not clear.

Attempted recrystallization of a sample of $Ti(NC_6F_5)Cl_2(py)_3$ (**15**) (generated in situ by an aniline/*tert*-butylimido exchange reaction[16] between $C_6F_5NH_2$ and $Ti(N^tBu)Cl_2(py)_3$) gave diffraction-quality crystals of the dimeric bis(pyridine) derivative $Ti_2(NC_6F_5)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (**17**) which was crystallographically characterized. Selected bond and intermolecular distances and bond angles are summarized in Table 4. A view of the molecular structure and a portion of the extended packing arrangement is shown in Figure 8. The loss of the *trans*-pyridine from **15** to form **17** is precedented as mentioned above and attributable to the strong trans influence of imido ligands.

Molecules of **17** lie across crystallographic inversion centers and are analogous to the previously reported homologues $Ti_2(NR)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (R = ^tBu, 2-C_6H_4R' (R′ = Me, ^tBu, or Ph)).[16,20] Unlike any of these other compounds, however, molecules of **17** show pronounced π-stacked supramolecular arrangements as shown in Figure 8, bottom. The π-interactions between the C_6F_5 rings give rise to infinite offset face-to-face arranged stacks propagating in the direction of the crystallographic *a* axis. Unlike the π-stacking arrangement for $Ti(NC_6F_5)Cl_2(NHMe_2)_2$ (**9**, Figure 6), that of **17** is different since the environments on either side of any individual C_6F_5 ring are not equivalent. For example the C_6F_5 ring is much less offset with respect to the

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(59) Adams, N.; Mountford, P. Unpublished results.

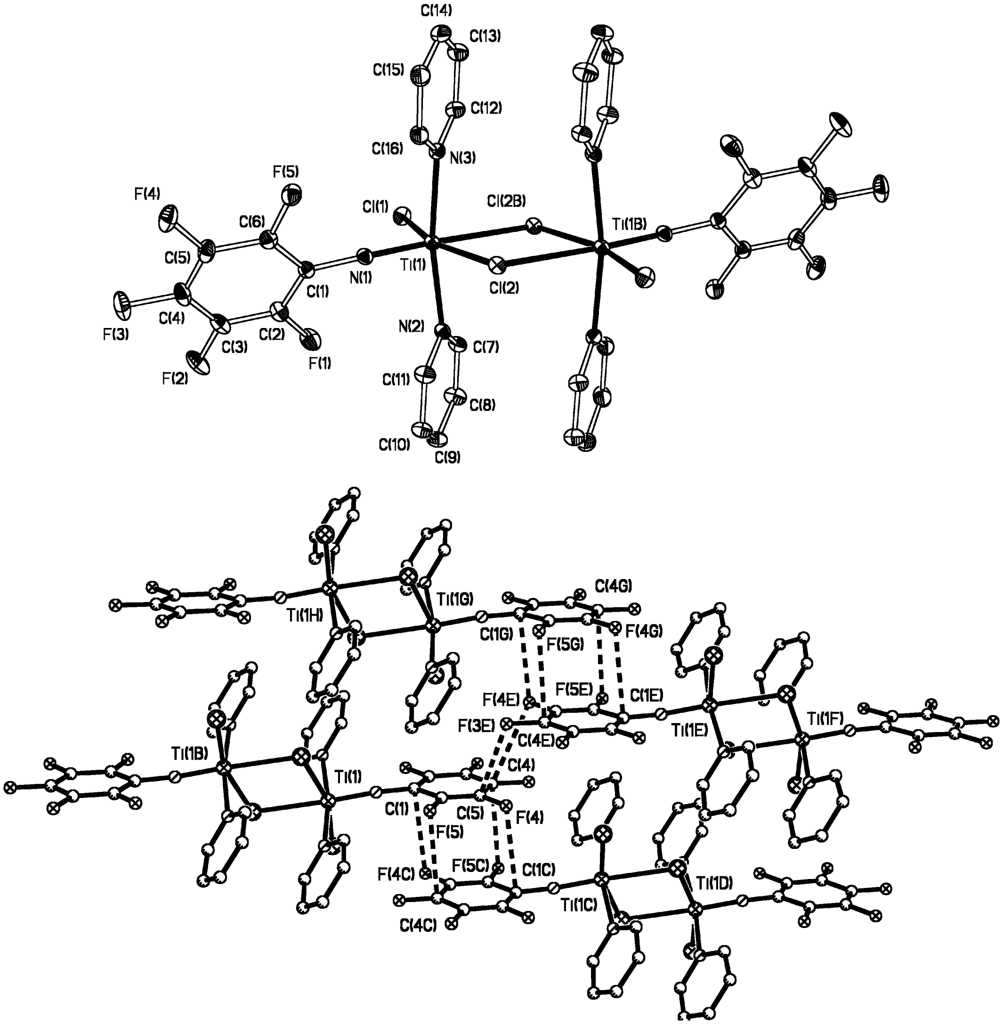

Figure 8. Top: Displacement ellipsoid plot of $Ti_2(NC_6F_5)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (**17**, 30% probability). H atoms are omitted. Atoms carrying the suffix B are related to their counterparts by the symmetry operator. Bottom: a portion of the infinite π-stacked chains. H atoms are omitted, and all atoms are drawn as spheres of arbitrary radius. Symmetry operators: B, $[1-x, -y, 1-z]$; C, $[1-x, -y, -z]$; D, $[x, y, z-1]$; E, $[-x, -y, -z]$; F, $[1+x, y, z-1]$; G, $[1+x, y, z]$, H $[2-x, -y, 1-z]$. The dashed lines indicate the closest intramolecular C⋯F distances (cf. Table 4).

$C(C)_6F(C)_5$ ring than with respect to the $C(E)_6F(E)_5$ ring. The shortest C⋯F contacts are between the more offset rings (e.g., C(5)⋯F(3E) = 3.068(5) and C(4)⋯F(4E) = 3.200(5) whereas C(4)⋯F(5C) = 3.303(5) and C(5)⋯C(6C) = 3.341(5) Å), possibly reflecting reduced electrostatic repulsions between ring π electron density in the more offset pairs.

Summary

Reaction of $Ti(NMe_2)_2Cl_2$ with primary aryl and alkylamines provides a robust and reliable route to the synthons $Ti(NR)Cl_2(NHMe_2)_2$ which are promising new entry points to certain new titanium imido compounds. An analogous reaction provides a useful route to a polystyrene-supported derivative. The supramolecular arrangements of six $Ti(NR)Cl_2(NHMe_2)_2$ compounds show a great deal of variation in the extent and type of interaction, with N−H⋯Cl hydrogen bonding being the dominant feature in the absence of perhalogenated imido N-aryl rings. This paper represents the first detailed study of how supramolecular structures of imido compounds may be influenced by simple variation of the imido ligand N-substituent. The substitution reactions of $Ti(NR)Cl_2(NHMe_2)_2$ with pyridine are not straightforward but do afford bis- and tris-pyridine derivatives in certain cases.

Experimental Section

General Methods and Instrumentation. All air- and moisture-sensitive operations were carried out using standard Schlenk-line (Ar) and drybox (N_2) techniques. Protio- and deutero-solvents were purified, dried, and distilled using conventional techniques. NMR samples were prepared under dinitrogen in Wilmad 505-PS tubes fitted with J. Young NMR/5 valves. Samples for MAS NMR spectroscopy were prepared in 2 mm Zirconia rotors. ^1H and ^{13}C-{1H} NMR spectra were recorded on Varian Unity Plus 500 and Varian Mercury-VX 300 spectrometers. Spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{19}F spectra were externally referenced to $CFCl_3$ ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. ^1H and ^{13}C-{^1H} MAS NMR spectra were recorded on a Chemagnetics 400 Infinity spectrometer. Spectra were referenced internally to tetramethylsilane. IR spectra were recorded on Perkin-Elmer 1600 and Perkin-Elmer 1710 spectrometers as Nujol mulls between KBr or NaCl windows, and in some instances as CH_2Cl_2 solutions using a 0.1 mm path length NaCl cell. All data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded on a Micromass GCT TOF instrument using a solid probe inlet temperature program. All data are quoted in mass/charge ratio (*m*/*z*). Elemental analyses were carried out by the analytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford.

Starting Materials. The compounds Ti(NMe$_2$)$_2$Cl$_2$[24] and Ti(N^{t}Bu)Cl$_2$(py)$_3$[16] were prepared according to the literature methods. Pyridine and liquid primary amines were predried over freshly ground CaH$_2$ and distilled prior to use. Aminomethyl polystyrene resin (Novabiochem; 100−200 mesh; loading, 1.19 mmol·g^{-1}) was washed extensively with benzene, THF, dichloromethane, and pentane (to remove any low molecular weight PS fractions) and dried under dynamic vacuum (1 × 10^{-3} mbar, 24 h) prior to use. All other compounds and reagents were purchased from commercial chemical suppliers and used without further purification.

Ti(NR)Cl$_2$(NHMe$_2$)$_2$ (1−13): General Synthetic Procedure. A solution of Ti(NMe$_2$)$_2$Cl$_2$ (ca. 1−5 mmol) and RNH$_2$ (1 equiv) in benzene (10−20 mL) was stirred for ca. 16 h. Removal of the volatiles under reduced pressure yielded the target compounds as spectroscopically pure air- and moisture-sensitive yellow or orange powders. Samples of the products were recrystallized from subsaturated benzene solution where necessary but were typically obtained in analytically pure form. Full details are provided in the Supporting Information.

(a) Data for 1 (R = ^{t}Bu). Yield = 84%. ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): 2.65 (2 H, br m, N*H*Me$_2$)**,** 2.24 (12 H, d, ^3J = 5.9 Hz, NH*Me*$_2$), 1.04 (9H, s, ^{t}Bu). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 72.1 (*C*Me$_3$), 40.3 (NHMe$_2$), 31.5 (C*Me*$_3$). IR (KBr plates, Nujol, cm^{-1}): 3231 (w), 1498 (w), 1352 (m), 1296 (m), 1260 (m), 1246 (m), 1206 (w), 1156 (w), 1074 (m), 1066 (m), 1012 (m), 1002 (m), 892 (w), 844 (w), 804 (m), 784 (m), 748 (w), 722 (s), 596 (w), 584 (w), 538 (m), 438 (w), 420 (w). Anal. found (calcd for C$_8$H$_{23}$Cl$_2$N$_3$Ti): C, 33.7 (34.3); H, 8.2 (8.3); N, 13.9 (15.0)%. Recrystallization did not lead to an improved % C, N analysis.

(b) Data for 2 (R = ^{i}Pr). Yield = 75%. ^{1}H NMR (C$_6$D$_6$, 500.1 MHz, 298 K): 3.29 (1H, sept, ^3J = 6.8 Hz, C*H*Me$_2$), 2.65 (2 H, br m, N*H*Me$_2$), 2.25 (12 H, d, ^3J = 6.4 Hz, NH*Me*$_2$), 0.94 (6 H, d, ^3J = 6.8 Hz, CH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 69.1 (*C*HMe$_2$), 40.5 (CH*Me*$_2$), 25.4 (NHMe$_2$). IR (KBr plates, Nujol, cm^{-1}): 3228 (m), 1402 (w), 1354 (w), 1298 (m), 1258 (m), 1240 (m), 1214 (w), 1146 (w), 1120 (m), 1108 (m), 1062(m), 1018 (m), 900 (m), 800 (w), 722 (m), 634 (m), 500 (m). IR (NaCl cell, CH$_2$Cl$_2$, ν(N−H), cm^{-1}): 3288. Anal. found (calcd for C$_7$H$_{21}$Cl$_2$N$_3$Ti): C, 31.4 (31.6); H, 7.9 (8.0); N, 15.5 (15.8)%. EI-MS: *m*/*z* = 266 (7%) [M]$^+$.

(c) Data for 3 (R = CH$_2$Ph). Yield = 62%. ^{1}H NMR (C$_6$D$_6$, 500.1 MHz, 298 K): 7.51 (2 H, d, ^3J = 7.3, 2-C$_6$H$_5$), 7.26 (2H, t, ^3J = 7.8, 3-C$_6$H$_5$), 7.10 (1 H, t, ^3J = 7.8, 4-C$_6$H$_5$), 4.37 (2 H, s, CH$_2$), 2.68 (2 H, br m, N*H*Me$_2$), 2.29 (12 H, d, ^3J = 6.4, NH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 141.7 (*i*-C$_6$H$_5$), 128.7 (2-C$_6$H$_5$), 127.1 (3-C$_6$H$_5$), 126.9 (4-C$_6$H$_5$), 72.8 (CH$_2$), 40.4 (NHMe$_2$). IR (KBr plates, Nujol, cm^{-1}): 3220 (w), 1333 (m), 1305 (w), 1260 (s), 1208 (w), 1152 (w), 1014 (s), 896 (s), 802 (m), 723 (s), 574 (w). Anal. found (calcd for C$_{11}$H$_{21}$Cl$_2$N$_3$Ti): C, 41.9 (42.1); H, 6.5 (6.7); N, 12.9 (13.3)%.

(d) Data for 4 (R = Ph). Yield = 95%. ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): 1 proton obscured under residual C$_6$D$_5$H, 7.02 (3 H, m, C$_6$H$_5$), 6.76 (1H, m, C$_6$H$_5$), 2.64 (2H, br m, N*H*Me$_2$), 2.23 (12 H, d, ^3J = 6.1 Hz, NH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 298 K): 161.0 (*i*-C$_6$H$_5$), 128.5 (2-C$_6$H$_5$), 123.7 (3-C$_6$H$_5$), 122.7 (4-C$_6$H$_5$), 40.4 (NHMe$_2$). IR (KBr plates, Nujol, cm^{-1}): 3220 (w), 1326 (m), 1258 (w), 1210 (w), 1018 (m), 894 (m), 750 (m), 722 (m), 688 (m), 658 (w), 644 (w), 604 (w), 590 (w), 566 (w), 558 (w), 518 (m), 494 (m), 454 (w). IR (NaCl cell, CH$_2$Cl$_2$, ν(N−H), cm^{-1}): 3284. Anal. found (calcd for C$_{10}$H$_{19}$Cl$_2$N$_3$Ti): C, 39.7 (40.1); H, 7.7 (6.4); N, 13.6 (14.0)%.

(e) Data for 5 (R = 2,6-C$_6$H$_3$Me$_2$). Yield = 84%. ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K): 6.89 (2 H, d, ^3J = 7.6 Hz, 3-C$_6$H$_3$Me$_2$), 6.79 (1 H, t, ^3J = 7.1 Hz, 4-C$_6$H$_3$Me$_2$), 2.75 (6 H, s, C$_6$H$_3$*Me*$_2$), 2.64 (2 H, br m, N*H*Me$_2$), 2.17 (12 H, d, ^3J = 6.1 Hz, NH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 160.3 (*i*-C$_6$H$_3$Me$_2$), 133.9 (2-C$_6$H$_3$Me$_2$), 127.5 (3-C$_6$H$_3$Me$_2$), 122.6 (4-C$_6$H$_3$Me$_2$), 40.7 (NHMe$_2$), 19.5 (C$_6$H$_3$*Me*$_2$). IR (KBr plates, Nujol, cm^{-1}): 3242 (m), 1305 (m), 126 (m), 1155 (w), 1123 (w), 1092 (w), 1014 (m), 899 (m), 802 (w), 769 (m), 738 (m), 723 (m). Anal. found (calcd for C$_{12}$H$_{23}$Cl$_2$N$_3$Ti): C, 44.0 (43.9); H, 7.8 (8.0); N, 12.4 (12.8)%.

(f) Data for 6 (R = 2,6-C$_6$H$_3$^{i}Pr$_2$). Yield = 86%. ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K): 6.99 (2 H, d, ^3J = 7.8 Hz, 3-C$_6$H$_3$^{i}Pr$_2$), 6.85 (1 H, app t, app ^3J = 7.3 Hz, 4-C$_6$H$_3$^{i}Pr$_2$), 4.65 (1 H, sept, ^3J = 6.4 Hz, C*H*Me$_2$), 2.87 (2 H, br m, N*H*Me$_2$), 2.22 (12 H, d, ^3J = 6.4 Hz, NH*Me*$_2$), 1.40 (12 H, d, ^3J = 6.8 Hz, HC*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 298 K): 157.6 (*i*-C$_6$H$_3$^{i}Pr$_2$), 144.5 (2-C$_6$H$_3$^{i}Pr$_2$), 123.6 (3-C$_6$H$_3$^{i}Pr$_2$), 122.5 (4-C$_6$H$_3$^{i}Pr$_2$), 40.6 (NHMe$_2$), 27.7 (*C*HMe$_2$), 24.4 (CH*Me*$_2$). IR (KBr plates, Nujol, cm^{-1}): 3244 (w), 1332 (w), 1308 (w), 1284 (w), 1212 (w), 1168 (w), 1156 (w), 1094 (m), 1054 (m), 1040 (m), 1020 (m), 986 (m), 932 (w), 864 (m), 798 (m), 752 (m), 722 (m). Anal. found (calcd for C$_{16}$H$_{31}$Cl$_2$N$_3$Ti): C, 49.8 (50.0); H, 8.3 (8.1); N, 10.8 (10.9)%.

(g) Data for 7 (R = 2,4,6-C$_6$H$_2$F$_3$). Yield = 92%. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): 6.18 (2H, dd, ^3J = 8.3 Hz, 3-C$_6$H$_2$F$_3$), 2.78 (2 H, m, N*H*Me$_2$), 2.25 (12 H, d, ^3J = 6.6 Hz, NH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): 99.5 (dd, ^2J = 29 Hz, ^2J = 26 Hz, 3-C$_6$H$_2$F$_3$), 40.8 (NMe$_2$). ^{13}C-{^{19}F} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): 158.1 (2-C$_6$H$_2$F$_3$), 155.5 (4-C$_6$H$_2$F$_3$), 135.6 (*i*-C$_6$H$_2$F$_3$).^{19}F NMR (C$_6$D$_6$, 282.4 MHz, 298 K): −120.84 (2 F, d,^3J = 7.6 Hz, 2-C$_6$H$_2$F$_3$), −115.33 (1 F, d,^3J = 9.0 Hz, 4-C$_6$H$_2$F$_3$). IR (NaCl plates, Nujol, cm^{-1}): 3244 (w), 1488 (m), 1312 (m), 1260 (m), 1118 (m), 1026 (m), 1012 (m), 984 (w), 896 (w), 830 (w), 806 (w), 722 (w). IR (NaCl cell, CH$_2$Cl$_2$, ν(N−H), cm^{-1}): 3282. Anal. found (calcd for C$_{10}$H$_{16}$Cl$_2$F$_3$N$_3$Ti): C, 33.8 (33.9); H, 4.5 (4.6); N, 11.7 (11.9)%.

(h) Data for 8 (R = 2,3,5,6-C$_6$HF$_4$). Yield = 86%. ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): 5.93 (1 H, m, 4-C$_6$HF$_4$), 2.72 (2 H, m, NHMe$_2$), 2.20 (12 H, d, ^3J = 6.0 Hz, NH*Me*$_2$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): 98.0 (t, ^2J = 23.3 Hz, 4-C$_6$HF$_4$), 41.0 (NMe$_2$). ^{13}C-{^{19}F} NMR (C$_6$D$_6$, 75.5 MHz, 298 K): 145.9 (d,^2J = 7.2 Hz, 2-C$_6$HF$_4$), 143.0 (d,^2J = 8.4 Hz, 3-C$_6$HF$_4$). ^{19}F NMR (C$_6$D$_6$, 282.4 MHz, 298 K): −154.52 (m, C$_6$HF$_4$), −142.29 (m, C$_6$HF$_4$). IR (NaCl plates, Nujol, cm^{-1}): 3258 (w), 1626 (m), 1586 (m), 1496 (s), 1378 (s), 1310 (m), 1112 (m), 1008 (m), 932 (m), 892 (m), 822 (m). IR (NaCl cell, CH$_2$Cl$_2$, ν(N−H), cm^{-1}): 3282. Anal. found (calcd for C$_{10}$H$_{16}$Cl$_2$F$_3$N$_3$Ti): C, 32.3 (32.3); H, 4.1 (4.1); N, 11.2 (11.3)%.

(i) Data for 9 (R = C$_6$F$_5$). Yield = 90%. ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): 2.67 (2H, br m, N*H*Me$_2$), 2.16 (12 H, d, ^3J = 6.1 Hz, NH*Me*$_2$). ^{19}F NMR (282.4 MHz, C$_6$D$_6$, 298 K): −155.28 (2 F, br d, ^3J = 22.8 Hz, 2-C$_6$F$_5$), −166.01 (2 F, dt, ^3J = 22.9 Hz, 3-C$_6$F$_5$), −166.86 (1 F, t, ^3J = 21.4 Hz, 4-C$_6$F$_5$). ^{13}C-{^{1}H and ^{19}F} NMR (C$_6$D$_6$, 75.4 MHz, 298 K): 143.2 (2-C$_6$F$_5$), 137.3 (3-C$_6$F$_5$), 136.5 (4-C$_6$F$_5$), 134.0 (*i*-C$_6$F$_5$), 40.9 (NHMe$_2$). IR (KBr plates, Nujol, cm^{-1}): 3275 (m), 1612 (m), 1338 (m), 1306 (m), 1249 (m), 1213 (m), 1156 (m), 1111 (m), 992 (m), 982 (m), 720 (s), 449 (m), 406 (m). IR (NaCl cell, CH$_2$Cl$_2$, ν(N−H), cm^{-1}): 3280. Anal. found (calcd for C$_{10}$H$_{12}$Cl$_2$F$_5$N$_3$Ti): C, 30.7 (30.8); H, 3.7 (3.6); N 10.6 (10.8)%. EI-MS: *m*/*z* = 598 (45%) [M − 2 NHMe$_2$]$_2$$^+$, 345 (10%) [M − NHMe$_2$]$^+$, 298 (12%) [M − 2 NHMe$_2$]$^+$.

(j) Data for 10 (R = 4-C_6H_4Cl). Yield = 98%. ^{1}H NMR (500.1 MHz, 298 K, C_6D_6): 6.98 (2 H, d, ^3J = 8.8 Hz, 3-C_6H_4Cl), 6.72 (2 H, d, ^3J = 6.6 Hz, 2-C_6H_4Cl), 2.54 (2 H, br m, $\mathrm{N}\mathit{H}\mathrm{Me_2}$), 2.18 (12 H, d, ^3J = 6.2 Hz, $\mathrm{NH}\mathit{Me_2}$). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K,): 158.9 (*i*-C_6H_4Cl), 128.6 (3-C_6H_4Cl), 127.6 (4-C_6H_4Cl), 125.0 (2-C_6H_4Cl), 40.5 ($NHMe_2$). IR (KBr plates, Nujol, cm^{-1}): 3228 (m), 1333 (m), 1261 (m), 1211 (w), 1167 (w), 1114 (m), 1091 (m), 1018 (s), 983 (m), 894 (m), 829 (m), 801 (m), 723 (s), 520 (w), 498 (w). Anal. Found (calcd for $C_{10}H_{18}Cl_2N_3Ti$): C, 35.9 (35.9); H, 5.3 (5.4); N, 12.9 (12.6)%.

(k) Data for 11 (R = 2,3,5,6-C_6HCl_4). Yield = 91%. ^{1}H NMR (C_6D_6, 499.9 MHz, 298 K): 6.67 (1 H, s, C_6HCl_4), 2.78 (2 H, br m, $\mathrm{N}\mathit{H}\mathrm{Me_2}$), 2.16 (12 H, d, ^3J = 5.9 Hz, $\mathrm{NH}\mathit{Me_2}$). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): 131.2 (C_6HCl_4), 128.5 (C_6HCl_4), 128.3 (C_6HCl_4), 123.3 (*p*-C_6HCl_4), 41.0 ($NHMe_2$). IR (KBr plates, Nujol, cm^{-1}): 3239 (w), 1304 (w), 1260 (s), 1210 (w), 1150 (w), 1095 (m), 1045 (m), 1022 (m), 1014 (m), 893 (m), 806 (m), 722 (s), 713 (m), 678 (m). IR (NaCl cell, CH_2Cl_2, ν(N−H), cm^{-1}): 3280. Anal. found (calcd for $C_{10}H_{15}Cl_6N_3Ti$): C, 27.1 (27.4); H, 3.9 (3.5); N, 9.3 (9.6)%.

(l) Data for 12 (R = 2-$C_6H_4CF_3$). Yield = 85%. ^{1}H NMR (C_6D_6, 499.9 MHz, 298 K): 7.27 (1 H, d, ^3J = 8.1 Hz, 3-$C_6H_4CF_3$), 7.21 (1 H, d, ^3J = 7.8 Hz, 6-$C_6H_4CF_3$), 6.95 (1 H, app t, app ^3J = 7.6 Hz, 5-$C_6H_4CF_3$), 6.49 (1 H, app t, app ^3J = 7.7 Hz, 4-$C_6H_4CF_3$), 2.72 (2 H, br m, $\mathrm{N}\mathit{H}\mathrm{Me_2}$), 2.20 (12 H, d, ^3J = 6.1 Hz, $\mathrm{NH}\mathit{Me_2}$). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): 156.4 (*i*- $C_6H_4CF_3$), 132.1(5-$C_6H_4CF_3$), 129.1 (6-$C_6H_4CF_3$), 125.9 (2-$C_6H_4CF_3$), 125.4 (3-$C_6H_4CF_3$), 121.7 (4-$C_6H_4CF_3$), 40.5 ($NHMe_2$), no signal observed for CF_3. IR (KBr plates, Nujol, cm^{-1}): 3264 (m), 2360 (w), 1592 (m), 1561 (m), 1342 (s), 1313 (s), 1251 (m), 1124 (s), 1055 (s), 1030 (s), 1002 (m), 894 (m), 802 (m), 756 (s), 503 (w). IR (NaCl cell, CH_2Cl_2, ν(N−H), cm^{-1}): 3284. Anal. found (calcd for $C_{11}H_{18}Cl_2F_3N_3Ti$): C, 35.3 (35.9); H, 4.9 (4.9); N, 11.2 (11.4)%. EI-MS: m/z = 281 (34%) $[M - 2\ Cl - CH_4]^+$, m/z = 207 (100%) $[M - 2\ Cl - 2\ NHMe_2]^+$.

(m) Data for 13 (R = 2-$C_6H_4{}^tBu$). Yield = 74%. ^{1}H NMR (C_6D_6, 499.9 MHz, 298 K): 7.83 (1 H, d, ^3J = 6.8 Hz, 6-$C_6H_4{}^tBu$), 7.16 (1 H, d, ^3J = 7.3 Hz, 3-$C_6H_4{}^tBu$), 7.04 (1 H, app t, app ^3J = 7.6 Hz, 5-$C_6H_4{}^tBu$), 6.78 (1 H, app t, app ^3J = 7.7 Hz, 4-$C_6H_4{}^tBu$), 2.76 (2 H, br m, $\mathrm{N}\mathit{H}\mathrm{Me_2}$), 2.20 (12 H, d, ^3J = 6.3 Hz, $\mathrm{NH}\mathit{Me_2}$), 1.68 (9 H, s, ^tBu). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 298 K): 160.2 (2-$C_6H_4{}^tBu$), 139.0 (*i*- $C_6H_4(^tBu)$), 133.3 (6-$C_6H_4{}^tBu$), 126.7 (4-$C_6H_4{}^tBu$), 125.4 (3-$C_6H_4{}^tBu$), 123.2 (5-$C_6H_4{}^tBu$), 40.3 ($NHMe_2$), 35.5 ($\mathit{C}\mathrm{Me_3}$), 30.8 ($\mathrm{C}\mathit{Me_3}$). IR (NaCl plates, Nujol, cm^{-1}): 3583 (w), 3273 (m), 3258 (m), 3205 (w), 1581 (w), 1427 (m), 1304 (s), 1261 (w), 1021 (m), 983 (m), 894 (m), 801 (w), 764 (m), 665 (m). IR (NaCl cell, CH_2Cl_2, ν(N−H), cm^{-1}): 3285. Anal. found (calcd for $C_{14}H_{27}Cl_2N_3Ti$): C, 46.2 (47.2); H, 6.8 (7.6); N, 11.3 (11.8)%. EI-MS: m/z = 265 (12%) $[M - 2\ NHMe_2]^+$, m/z = 134 (100%) $[M - Ti - 2\ NHMe_2 - 2\ Cl]^+$.

Alternative Synthesis of $Ti(N\text{-}2\text{-}C_6H_4{}^tBu)Cl_2(NHMe_2)_2$ (13). To a yellow solution of $Ti(NMe_2)_4$ (0.18 g, 0.82 mmol) in toluene (10 cm^3) was added 2-*tert*-butyl aniline (0.13 g, 0.82 mmol) and trimethylsilyl chloride (0.42 cm^3, 3.3 mmol) via microliter syringe. The yellow solution immediately darkened to orange. The mixture was stirred at 80 °C for 1 h and filtered, and volatiles were removed under reduced pressure. The product was obtained as a brown powder. Yield: 0.21 g (72%).

$Ti(N{-}CH_2\text{-}4\text{-}C_6H_4PS)Cl_2(NHMe_2)_2$ (14). Aminomethyl polystyrene resin (1.57 g; loading 1.19 $mmol{\cdot}g^{-1}$, 1.87 mmol) was preswollen in benzene (20 mL) for 30 min. A deep orange solution of $Ti(NMe)_2Cl_2$ (0.39 g, 1.87 mmol) in benzene (10 mL) was added, and the mixture was shaken at room temperature for 16 h. Soon after addition, the solution started to discolor and the initially off-white resin took on a red-brown color. The resin was filtered off and washed with benzene (5 × 10 mL) and hexanes (3 × 10 mL) and dried in vacuo to afford a red-brown material. Yield: 1.862 g (95%). ^{1}H MAS NMR (399.9 MHz, 298 K, 4 kHz, swollen in $CDCl_3$): 7.1 (v br, PS resin aromatic H), 6.5 (v br, PS resin aromatic H), 4.3 (br, $\mathrm{PhC}\mathit{H_2}\mathrm{N{=}Ti}$), 3.3 (br, $\mathrm{N}\mathit{H}\mathrm{Me_2}$), 2.5 (br, $\mathrm{NH}\mathit{Me_2}$), 1.8 (v br, PS resin aliphatic H), 1.4 (v br, PS resin aliphatic H). ^{13}C-{^{1}H} MAS NMR (100.6 MHz, 298 K, 4 kHz, swollen in $CDCl_3$): 144.9 (br, PS resin aromatic C), 127.6 (v br, PS resin aromatic C), 125.4 (v br, PS resin aromatic C), 72.9 (br, $\mathrm{Ph}\mathit{C}\mathrm{H_2N{=}Ti}$), 45.7 (v br, PS resin aliphatic C), 43.5 (v br, PS resin aliphatic C), 40.3 (v br (overlapping), PS resin aliphatic C and $\mathrm{HN}\mathit{Me_2}$). IR (KBr pellet, cm^{-1}): 3268 (s), 3082 (s), 3055 (s), 3025 (s), 2972 (s), 2920 (s), 2848 (s), 2800 (s), 1946 (m), 1872 (m), 1814 (m), 1748 (w), 1646 (w), 1600 (s), 1582 (s), 1492 (s), 1450 (s), 1478 (s), 1400(m), 1372 (m), 1324 (m), 1246 (m), 1180 (m), 1154 (m), 1118 (m), 1068 (m), 1020 (s), 982 (s), 892 (s), 842 (m), 822 (m), 758 (s), 672 (s), 534 (s). Despite our best efforts, elemental analysis of the product repeatedly returned lower than expected %N, Cl, and Ti values. This is attributed to incomplete combustion or acid digestion. The spectroscopic data and other experimental observations (see Results and Discussion above) are consistent with quantitative uptake of $Ti(NMe_2)_2Cl_2$ to form the desired **14**.

$Ti_2(N^tBu)_2Cl_2(\mu\text{-}Cl)_2(py)_4$. A solution of $Ti(N^tBu)Cl_2(NHMe_2)_2$ (0.100 g, 0.357 mmol) in pyridine (5.0 mL, 62 mmol) was heated at 80 °C for 16 h. The solution was concentrated to three-quarters of the original volume, dichloromethane (15 mL) was added, and the solution was filtered. Hexanes (20 mL) were added to the filtrate which resulted in the formation of an orange precipitate which was washed with hexanes (2 × 10 mL) and dried in vacuo to give an orange powder. Yield: 59 mg (48%). The ^{1}H NMR spectrum of the product confirmed the formation of spectroscopically pure $Ti_2(N^tBu)_2Cl_2(\mu\text{-}Cl_2)(py)_4$.[16]

$Ti(NC_6F_5)Cl_2(py)_3$ (15). A solution of $Ti(NC_6F_5)Cl_2(NHMe_2)_2Cl_2$ (0.300 g, 0.769 mmol) in pyridine (5.0 mL, 62 mmol) was heated at 80 °C for 16 h. After cooling to room temperature, hexanes (40 mL) were added and the mixture was stored at −15 °C for 16 h. The supernatant was decanted, and the solids were washed with hexanes (3 × 15 mL) and dried in vacuo to afford **15** as a yellow powder. Yield: 325 mg (89%). ^{1}H NMR ($CDCl_3$, 500.0 MHz, 298 K): 9.21 (4 H, d, J = 4.5 Hz, *o-cis*-NC_5H_5), 8.77 (2 H, br s, *o-trans*-NC_5H_5), 7.88 (2 H, apparent t, J = 7.5 Hz, *p-cis*-NC_5H_5), 7.71 (1 H, br s, *p-trans*-NC_5H_5), 7.42 (4 H, t, J = 6.5 Hz, *m-cis*-NC_5H_5), 7.29 (2 H, br s, *m-cis*-NC_5H_5). ^{13}C-{^{1}H} NMR ($CDCl_3$, 125.7 MHz, 298 K): 152.1 (*o-cis*-NC_5H_5), 150.9 (*o-trans*-NC_5H_5), 138.9 (*p-cis*-NC_5H_5), 137.4 (*p-trans*-NC_5H_5), 124.0 (*m-cis*-NC_5H_5), 123.7 (*m-trans*-CN_5H_5). Resonances for C_6F_5 not observed. ^{19}F NMR ($CDCl_3$, 282.4 MHz, 298 K): −153.1 (2 F, d, J = 22.9 Hz, *o*-C_6F_5), −166.8 (2 F, apparent t, J = 19.8 Hz, *m*-C_6F_5), −166.9 (1 F, br s, *p*-C_6F_5). IR (KBr plates, Nujol mull, cm^{-1}): 3630 (w), 2454 (w), 1800 (s), 1716 (s, br), 1568 (m), 1538 (w), 1264 (m), 1196 (m, br), 1166 (w), 1056 (m, br), 826 (m), 660 (m), 428 (w). Anal. found (calcd for $C_{21}H_{15}Cl_2F_5N_4Ti$): C, 47.0 (47.0); H, 3.1 (2.8); N, 10.5 (10.4)%.

$Ti(N\text{-}4\text{-}C_6H_4Cl)Cl_2(py)_3$ (16). A solution of $Ti(N\text{-}4\text{-}C_6H_4Cl)Cl_2(NHMe_2)_2$ (0.300 g, 0.897 mmol) in pyridine (5.0 mL, 62 mmol) was heated at 80 °C for 16 h and then cooled to 0 °C. Hexanes (20 mL) were added, and the resultant solids were washed with hexanes (2 × 20 mL) and dried in vacuo to afford **16** as a brown powder. Yield: 384 mg (89%). The *trans*-pyridine is fairly labile, and some loss was always encountered during the drying process. This is reflected in the elemental analysis. ^{1}H NMR ($CDCl_3$, 500.0 MHz, 298 K): 9.06 (4 H, d, $J = 5.5$ Hz, *o-cis*-NC_5H_5), 8.78 (2 H, br s, *o-trans*-NC_5H_5), 7.80 (2 H, t, $J = 7$ Hz, *p-cis*-NC_5H_5), 7.68 (1 H, br s, *p-trans*-NC_5H_5), 7.47 (4 H, t, $J = 7.0$ Hz, *m-cis*-NC_5H_5), 7.34 (2 H, apparent t, apparent $J = 6.5$ Hz, *m-trans*-NC_5H_5), 6.96 (2 H, d, $J = 8.0$ Hz, *m*-C_6H_4Cl), 6.84 (2 H, d, $J = 8.0$ Hz, *o*-C_6H_4Cl). $^{13}C\text{-}\{^1H\}$ ($CDCl_3$, 125.7 MHz, 298 K): 151.4 (*o-cis*-NC_5H_5), 150.9 (*o-trans*-NC_5H_5), 138.7 (*p-cis*-NC_5H_5), 136.9 (*p-trans*-NC_5H_5), 157.1, 128.0, 124.9 (*o*-, *m*-, and *p*-C_6H_4Cl), 124.1 (*m-cis*-NC_5H_5), 123.8 (*m-trans*-NC_5H_5). Resonance for *ipso*-C_6H_4Cl not observed. IR (KBr plates, Nujol mull, cm^{-1}): 2724 (w), 2670 (w), 1602 (s), 1568 (w), 1328 (m), 1306 (w, br), 1262 (w), 1222 (w), 1212 (s), 1148 (m), 1090 (m), 1062 (s), 1042 (s), 1012 (m), 968 (w), 936 (w), 830 (s), 760 (m), 750 (m), 692 (s), 638 (s), 622 (w), 518 (s), 432 (m). Anal. found (calcd for $C_{18.5}H_{16.5}Cl_3N_{3.5}Ti$): C, 50.2 (50.3); H, 3.8 (4.2); N, 11.1 (11.1)%.

$Ti_2(NC_6F_5)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (17). To a solution of $Ti(NC_6F_5)Cl_2(py)_3$ (**15**, prepared in situ from $Ti(N^tBu)Cl_2(py)_3$ (0.300 g, 0.702 mmol) and $C_6F_5NH_2$ (0.128 g, 0.702 mmol) in dichloromethane) in dichloromethane (30 mL) was added pyridine (1.0 mL), and the mixture was carefully layered with hexanes. After 48 h at room temperature, dark yellow, diffraction-quality crystals were formed which were washed with hexanes (2 × 10 mL) and dried in vacuo. Yield: 71 mg (22%). ^{19}F NMR (NC_5D_5, 282.4 MHz, 298 K): -153.6 (2 F, d, $J = 22.9$ Hz, *o*-C_6F_5), -167.3 (2 F, t, $J = 21.5$ Hz, *m*-C_6F_5), -169.8 (1 F, t, $J = 21.2$ Hz, *p*-C_6F_5). IR (KBr plates, Nujol mull, cm^{-1}): 1606 (s), 1506 (s, br), 1494 (w, br), 1350 (w), 1326 (s), 1260 (m, br), 1218 (s, br), 1068 (m), 1048 (s, br), 1016 (m), 986 (s), 800 (w, br), 752 (m), 720 (w), 692 (s), 640 (s), 504 (w), 464 (w), 416 (m). Anal. found (calcd for $C_{32}H_{20}Cl_4F_{10}N_6Ti_2$): C, 41.5 (41.2); H, 2.2 (2.2); N, 9.1 (9.2)%. (The very insoluble crystals of **17** could only be dissolved in pydrine-d_5 making ^1H and ^{13}C spectra meaningless as they showed only resonances for $NC_5H_xD_{5-x}$.)

Crystal Structure Determinations of $Ti(NR)Cl_2(NHMe_2)_2$ (R = ^{i}Pr (2), Ph (4), C_6F_5 (9), 2-$C_6H_4CF_3$ (12)), Ti(N-2,3,5,6-C_6HCl_4)$Cl_2(NHMe_2)_2\cdot 0.5(C_6H_6)$ (11·0.5(C_6H_6)), Ti(N-2-$C_6H_4{}^tBu$)$Cl_2(NHMe_2)_2\cdot 0.5(C_5H_{12})$ (13·0.5(C_5H_{12})), and $Ti_2(NC_6F_5)_2Cl_2(\mu\text{-}Cl)_2(py)_4$ (17). Crystal data collection and processing parameters are given in Table 3. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using either an Enraf-Nonius DIP2000, KappaCCD, or MACH3 diffractometer. Intensity data were processed using either the RC93 program[60] or the DENZO-SMN package.[61] The structures were solved using the direct-methods program SIR92,[62] which located all non-hydrogen atoms. Additional electron density for **11·0.5(C_6H_6)** and **13·0.5(C_5H_{12})** was modeled as residual solvent of crystallization (benzene and pentane, respectively) disordered across crystallographic inversion centers. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[63] For **2**, **4**, and **9**, systematic absences were consistent with either *Cc* or *C*2/*c*. Comparison of the molecular structures obtained in the two spacegroups, along with the more successful structure solution and refinement in the latter, favored the centrosymmetric alternative. The compound **12** was satisfactorily solved and refined in the spacegroup $Pna2_1$ (as opposed to the centrosymmetric alternative *Pnam*) and found to contain two molecules in each asymmetric unit related by a noncrystallographic center of inversion. Refinement of the Flack enantiopole parameter[64] gave a value of 0.47(4), showing the crystal to be an inversion twin which is attributed to the locally centrosymmetric packing.

Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined (with the exception of the C atoms of the disordered benzene of crystallization in **11·0.5(C_6H_6)** which were refined isotropically subject to bond length and angle restraints). H atoms bonded to C were placed geometrically, as were the N−H atoms (N−H = 0.87 Å) in **2**, **4**, **9**, and **11·0.5C_6H_6**. For **13·0.5(C_5H_{12})** and **12** the N−H atoms could be located from Fourier difference maps and refined isotropically. However, for the purposes of geometric comparisons with **1**, **4**, **9**, and **11**, N−H distances of 0.87 Å were again used (for example in Table 2). Finally, weighting schemes and secondary extinction correction were applied as appropriate. A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, Issue No. 1.

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Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of **2**, **4**, **9**, **12**, **11·0.5(C_6H_6)**, **13·0.5(C_5H_{12})**, and **17**; full synthetic procedures for compounds **1**−**13**; cell packing diagram for **2**; views of **4**, **9**, and **12** projected onto the aryl ring carbons best-fit least-squares planes; plot of the other crystallographically independent molecule of **12**; space-filling representations of **12** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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