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Synthesis, Structures, and Reactions of Titanium, Scandium, and Yttrium Complexes of Diamino-bis(phenolate) Ligands: Monomeric, Dimeric, Neutral, Cationic, and Multiply Bonded Derivatives

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New groups 3 and 4 organometallic and coordination compounds supported by the tetradentate diamino-bis(phenolate) ligands $O_2{}^{tBu}NN'$ and $O_2{}^{Me}NN'$ are reported [$H_2O_2{}^{R}NN'$ = $(2\text{-}C_5H_4N)CH_2N(2\text{-}HO\text{-}3,5\text{-}C_6H_2R_2)_2$ where R = ${}^{t}Bu$ or Me] along with some comparative studies with the tridentate amino-bis(phenolate) ligand $O_2{}^{tBu}N$ ($H_2O_2{}^{tBu}N$ = ${}^{n}PrN(2\text{-}HO\text{-}3,5\text{-}C_6H_2{}^{t}Bu_2)_2$). Reaction of $Na_2O_2{}^{tBu}NN'$ with $ScCl_3$ and pyridine in THF gave monomeric $Sc(O_2{}^{tBu}NN')Cl(py)$ (**2**), whereas $Na_2O_2{}^{Me}NN'$ gave the dimeric phenoxy-bridged $Sc_2(O_2{}^{Me}NN')_2Cl_2$ (**3**). Reaction of $Na_2O_2{}^{tBu}NN'$ and YCl_3 in neat pyridine gave the chloride-bridged, seven-coordinate dimer $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2$ (**4**). Reaction of $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc or Y) with $H_2O_2{}^{tBu}NN'$ afforded $M(O_2{}^{tBu}NN')(CH_2SiMe_3)(THF)$. The one-pot reaction of $ScCl_3$ with $Na_2O_2{}^{R}NN'$ (R = ${}^{t}Bu$ or Me) and $Li[PhC(NSiMe_3)_2]$ gave the fluxional benzamidinate derivatives $Sc(O_2{}^{R}NN')\{PhC(NSiMe_3)_2\}$. Treatment of $Ti(NMe_2)_4$ with $H_2O_2{}^{R}NN'$ gave the corresponding $Ti(O_2{}^{R}NN')(NMe_2)_2$ (R = ${}^{t}Bu$ (**11**) or Me); **11** in turn reacts with HS-4-C_6H_4Me to give $Ti(O_2{}^{tBu}NN')(NMe_2)(S\text{-}4\text{-}C_6H_4Me)$. One-pot reactions of $TiCl_4(THF)_2$ with MeLi (2 equiv) followed by $H_2O_2{}^{R}NN'$ affords $Ti(O_2{}^{R}NN')Cl_2$ (R = ${}^{t}Bu$ (**9**) or Me (**10**)), which are cleanly methylated with MeMgBr to yield the corresponding $Ti(O_2{}^{R}NN')Me_2$ (R = ${}^{t}Bu$ (**14**) or Me (**15**)). The terminal imidotitanium compounds $Ti(O_2{}^{tBu}NN')(NR)(py)$ (R = ${}^{t}Bu$ or 2,6-$C_6H_3Me_2$) were formed from the respective $Ti(NR)Cl_2(py)_3$ reagents and $Na_2O_2{}^{tBu}NN'$, and these react with CO_2 by imido group transfer to yield the μ-oxo dimer $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2$ (**18**) and RNCO. The related five-coordinate compounds $Ti(O_2{}^{tBu}N)(NR)(py)$ (R = ${}^{t}Bu$, 2,6-$C_6H_3Me_2$ (**20**) or 2,6-$C_6H_3{}^{i}Pr_2$ (**21**)) were prepared in an analogous manner. These do not give identifiable metal products with CO_2. Treatment of the dimethyl compounds **14** or **15** with $B(Ar^F)_3$ or $[CPh_3][B(Ar^F)_4]$ (Ar^F = C_6F_5) gave the fluxional, dimeric phenoxy-bridged cations $[Ti_2(O_2{}^{R}NN')_2Me_2]^{2+}$, which show very sluggish 1-hexene polymerization behavior. The compounds **2**, **3**, **4**, **11**, **9**, **10**, **16**, **18**, **20**, and **21** have been crystallographically characterized.

Introduction

In the drive to extend the non-metallocene chemistry of the early to mid-transition elements, much progress has been made with mono- and polyanionic N-donor ligands.[1−4] One of our contributions has been to introduce the diamino-diamide ligands $(2\text{-}C_5H_4N)CH_2N(CH_2CH_2NSiMe_2R)_2$ (abbreviated as N_2NN' where R = Me or ${}^{t}Bu$).[5,6] These dianionic, tetradentate ligands can be useful supporting environments for groups 3, 4, and 5, six- and five-coordinate complexes of the general type $M(A)(B)(N_2NN')$ and $M(A)(N_2NN')$ (**I**, Chart 1). However, some of the reaction chemistry of these systems has been hampered by side-reactions involving the amido N-substituents, and for this reason we have been developing parallel studies with the corresponding diamino-bis(phenoxide) ligands $O_2{}^{R}NN'$ (R = ${}^{t}Bu$ or Me; see Chart 1). We recently reported in full the synthesis and structures of a range of neutral and cationic

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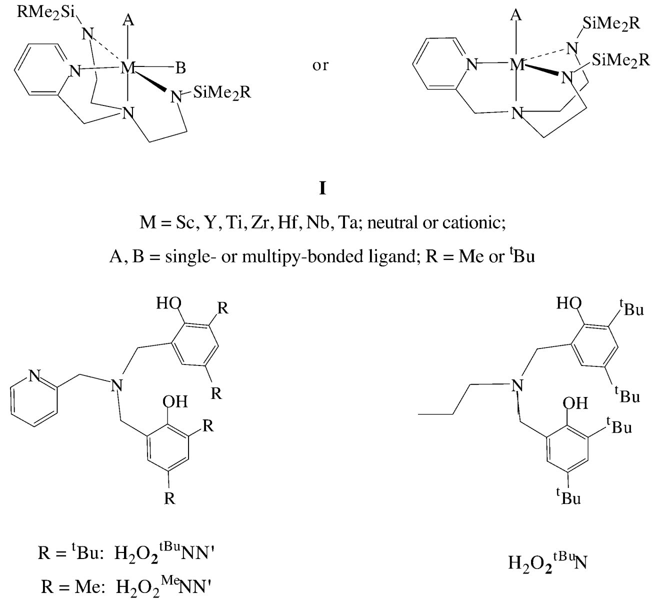
Chart 1



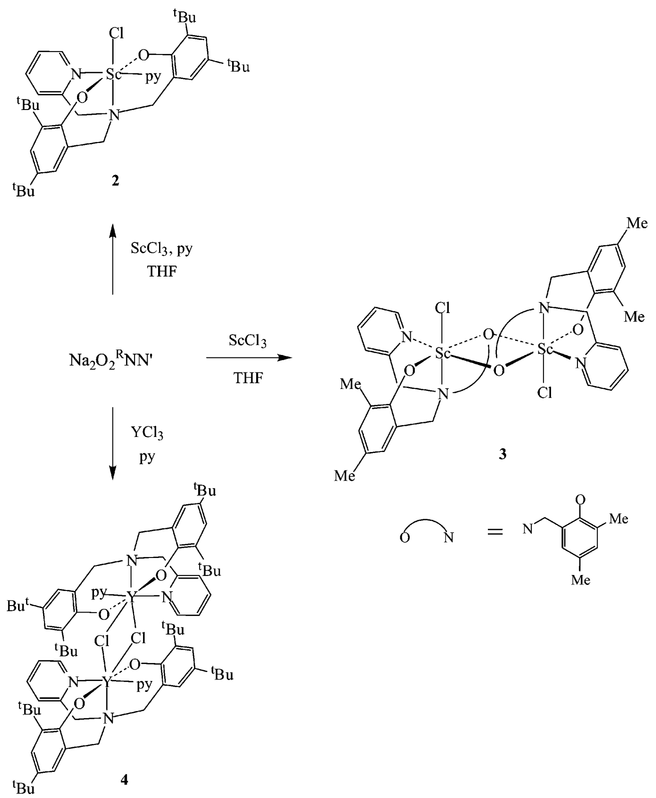
M = Sc, Y, Ti, Zr, Hf, Nb, Ta; neutral or cationic;

A, B = single- or multipy-bonded ligand; R = Me or ^{t}Bu

zirconium organometallic complexes with these ligands.[7] Kol et al. have reported extensively on olefin polymerization (in some instances living) by titanium and zirconium dibenzyls supported by ligands related to $O_2{}^RNN'$ but almost exclusively with the pyridyl moiety replaced by etheral O- or tertiary amino N-donors.[8−14] We were the first to use the $O_2{}^RNN'$ ligand in group 3,[15] and more recently Carpentier[16] and Kerton[17] have applied other members of this family (i.e., other donors in place of pyridyl) in catalytic studies using group 3 and lanthanide derivatives. A range of other dianionic O_2N_2-donor ligands have been applied recently (sometimes with great effect) in groups 3 and 4 and lanthanide chemistry.[2,3,18,19]

In this contribution we report our studies of the synthesis. structures, and selected reactions of new scandium, yttrium, and titanium compounds containing the $O_2{}^RNN'$ ligands. In one instance comparative studies have been made for the tridentate analogue $O_2{}^{tBu}N$ (see Chart 1). Part of this work has been communicated.[15]

Scheme 1. Synthesis of Group 3 Chloride Complexes of $O_2{}^RNN'$ (R = Me or ^{t}Bu)



Results and Discussion

The protio ligands (Chart 1) $H_2O_2{}^RNN'$ (R = ^{t}Bu[20] and Me[7]) and $H_2O_2{}^{tBu}N$[10] were prepared according to methods described by us and others. The sodium salts $Na_2O_2{}^RNN'$ were prepared by our previously reported methods,[7] namely, reaction of $H_2O_2{}^RNN'$ with NaH (2 equiv) in THF. The spectroscopically pure compound $Na_2O_2{}^{tBu}N$ (**1**) was prepared in an analogous way (92% yield), and an analytically pure form ($Na_2O_2{}^{tBu}N{\cdot}THF$) was obtained from THF/pentane. It is likely that all three sodium compounds exist as multiples of the simple formula units given here, but without structural data is it neither possible nor appropriate to comment further.

Scandium and Yttrium Complexes of $O_2{}^RNN'$. The new chemistry is summarized in Scheme 1. Reaction of $Na_2O_2{}^{tBu}NN'$ with either $ScCl_3$ or preformed $ScCl_3(THF)_3$ in THF afforded mixtures of products, which appeared from their NMR spectra to contain both C_s and C_1 symmetric species. The relative composition of the mixtures changed with handling (i.e., evaporation, re-extraction), and we speculated that THF loss might be occurring. Repeating the reaction with the addition

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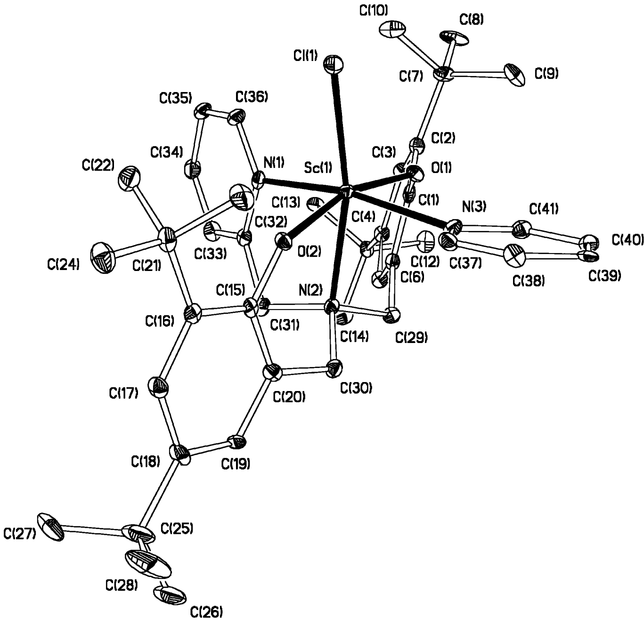

Figure 1. Displacement ellipsoid plot (20% probability) of $Sc(O_2{}^{tBu}NN')Cl(py)\cdot C_6H_6$ ($\mathbf{2}\cdot C_6H_6$). H atoms and C_6H_6 molecule of crystallization omitted for clarity.

of pyridine (Scheme 1) led to the single monomeric, C_s symmetric six-coordinate pyridine adduct $Sc(O_2{}^{tBu}NN')Cl(py)$ (**2**) in 59% yield after crystallization from benzene. The X-ray molecular structure is shown in Figure 1, and selected bond lengths are listed in Table 1. The structure confirms that given in Scheme 1 and will be discussed further below. Application of prolonged dynamic vacuum to **2** lead to pyridine loss and the appearance of a second (C_1 symmetric) species. The mixtures could always be converted back to pure **2** on the addition of pyridine, but a pure pyridine-free sample could not be isolated free of **2**.

Reaction of $Na_2O_2{}^{Me}NN'$ (a sterically less demanding ligand) with $ScCl_3$ in THF gave the base-free dimeric complex $Sc_2(O_2{}^{Me}NN')_2Cl_2$ (**3**) in 45% recrystallized yield.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Sc(O_2{}^{tBu}NN')Cl(py)$ (2)

Sc(1)−Cl(1)	2.431(2)	Sc(1)−N(1)	2.303(6)
Sc(1)−N(2)	2.381(5)	Sc(1)−N(3)	2.310(5)
Sc(1)−O(1)	2.002(4)	Sc(1)−O(2)	1.968(4)
O(1)−C(1)	1.354(7)	O(2)−C(15)	1.329(7)
Cl(1)−Sc(1)−N(1)	96.3(2)	Cl(1)−Sc(1)−N(2)	167.66(14)
N(1)−Sc(1)−N(2)	73.2(2)	Cl(1)−Sc(1)−N(3)	97.7(2)
N(1)−Sc(1)−N(3)	164.7(2)	N(2)−Sc(1)−N(3)	93.5(2)
Cl(1)−Sc(1)−O(1)	101.29(14)	N(1)−Sc(1)−O(1)	86.2(2)
N(2)−Sc(1)−O(1)	84.8(2)	N(3)−Sc(1)−O(1)	85.1(2)
Cl(1)−Sc(1)−O(2)	94.78(14)	N(1)−Sc(1)−O(2)	96.8(2)
N(2)−Sc(1)−O(2)	80.4(2)	N(3)−Sc(1)−O(2)	88.0(2)
O(1)−Sc(1)−O(2)	163.2(2)	Sc(1)−N(1)−C(32)	117.4(4)
Sc(1)−O(1)−C(1)	129.5(4)	Sc(1)−O(2)−C(15)	144.6(4)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Sc_2(O_2{}^{Me}NN')_2Cl_2$ (3)

Sc(1)−O(1)	2.1222(12)	Sc(1)−O(1A)	2.1386(13)
Sc(1)−O(2)	1.9443(13)	Sc(1)−N(1)	2.386(2)
Sc(1)−N(2)	2.387(2)	Sc(1)−Cl(1)	2.4269(5)
O(1)−C(1)	1.378(2)	O(2)−C(10)	1.342(2)
O(1)−Sc(1)−O(1A)	72.98(5)	O(1)−Sc(1)−O(2)	155.09(5)
O(1A)−Sc(1)−O(2)	94.44(5)	O(1)−Sc(1)−N(1)	88.96(5)
O(1A)−Sc(1)−N(1)	161.00(5)	O(2)−Sc(1)−N(1)	104.52(6)
O(1)−Sc(1)−N(2)	84.06(5)	O(1A)−Sc(1)−N(2)	111.78(5)
O(2)−Sc(1)−N(2)	80.82(5)	N(1)−Sc(1)−N(2)	71.03(5)
O(1)−Sc(1)−Cl(1)	100.53(4)	O(1A)−Sc(1)−Cl(1)	93.57(4)
O(2)−Sc(1)−Cl(1)	101.68(4)	N(1)−Sc(1)−Cl(1)	83.77(4)
N(2)−Sc(1)−Cl(1)	154.36(4)	Sc(1)−O(1)−Sc(1A)	107.02(5)
Sc(1)−O(1)−C(1)	118.8(1)	Sc(1A)−O(1)−C(1)	131.7(1)
Sc(1)−O(2)−C(10)	142.32(12)	Sc(1)−O(1A)−C(1A)	131.6(1)

The X-ray molecular structure is shown in Figure 2, and selected metric parameters are summarized in Table 2; these will be discussed further below. For the larger congener yttrium, only the reaction of YCl_3 with $Na_2O_2{}^{tBu}NN'$ afforded a single product, and again pyridine (this time as solvent) was required in order to obtain a single well-defined product. Thus the dimeric complex $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2$ (**4**) was isolated in 74% yield as a bright white powder after recrystallization from benzene/pentane. The X-ray molecular structure is shown in Figure 3, and distances and angles associated with the two yttrium centers are listed in Table 3.

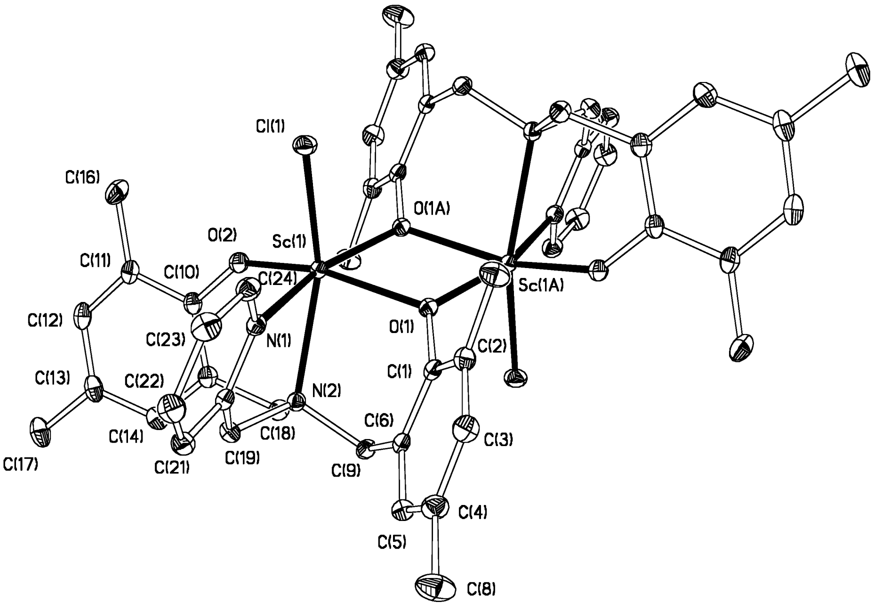

Figure 2. Displacement ellipsoid plot (35% probability) of $Sc_2(O_2{}^{Me}NN')_2Cl_2\cdot 2CH_2Cl_2$ ($\mathbf{3}\cdot 2CH_2Cl_2$). H atoms and CH_2Cl_2 molecules of crystallization omitted for clarity.

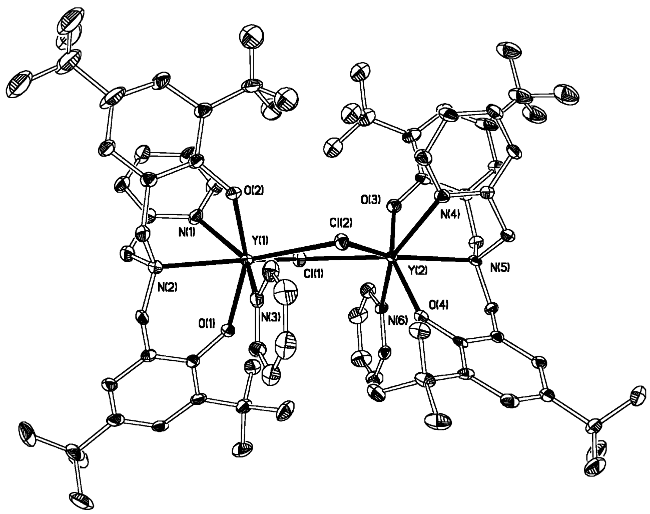

Figure 3. Displacement ellipsoid plot (25% probability) of $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2\cdot3(C_6H_6)$ (**4**·$3C_6H_6$). H atoms and C_6H_6 molecules of crystallization omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2$ (4)

Y(1)−Cl(1)	2.744(2)	Y(1)−Cl(2)	2.789(2)
Y(2)−Cl(1)	2.792(2)	Y(2)−Cl(2)	2.740(2)
Y(1)−O(1)	2.139(5)	Y(1)−O(2)	2.155(6)
Y(2)−O(3)	2.152(6)	Y(2)−O(4)	2.132(6)
Y(1)−N(1)	2.520(7)	Y(1)−N(2)	2.595(7)
Y(1)−N(3)	2.534(7)	Y(2)−N(4)	2.486(7)
Y(2)−N(5)	2.594(7)	Y(2)−N(6)	2.512(6)
Cl(1)−Y(1)−Cl(2)	71.91(7)	Cl(1)−Y(2)−Cl(2)	71.93(7)
Cl(1)−Y(1)−O(1)	87.1(2)	Cl(1)−Y(2)−O(3)	84.1(2)
Cl(2)−Y(1)−O(1)	118.1(2)	Cl(2)−Y(2)−O(3)	120.4(2)
Cl(1)−Y(1)−O(2)	119.8(2)	Cl(1)−Y(2)−O(4)	117.4(2)
Cl(2)−Y(1)−O(2)	82.3(2)	Cl(2)−Y(2)−O(4)	86.4(2)
O(1)−Y(1)−O(2)	151.3(2)	O(3)−Y(2)−O(4)	150.9(2)
Cl(1)−Y(1)−N(1)	78.3(2)	Cl(1)−Y(2)−N(4)	131.9(2)
Cl(2)−Y(1)−N(1)	129.6(2)	Cl(2)−Y(2)−N(4)	79.4(2)
O(1)−Y(1)−N(1)	99.5(2)	O(3)−Y(2)−N(4)	78.1(2)
O(2)−Y(1)−N(1)	78.4(2)	O(4)−Y(2)−N(4)	97.9(2)
Cl(1)−Y(1)−N(2)	137.1(2)	Cl(1)−Y(2)−N(5)	149.2(2)
Cl(2)−Y(1)−N(2)	150.6(2)	Cl(2)−Y(2)−N(5)	138.8(2)
O(1)−Y(1)−N(2)	75.0(2)	O(3)−Y(2)−N(5)	77.3(2)
O(2)−Y(1)−N(2)	78.0(2)	O(4)−Y(2)−N(5)	74.6(2)
N(1)−Y(1)−N(2)	67.1(2)	N(4)−Y(2)−N(5)	67.8(2)
Cl(1)−Y(1)−N(3)	133.3(2)	Cl(1)−Y(2)−N(6)	72.5(2)
Cl(2)−Y(1)−N(3)	74.0(2)	Cl(2)−Y(2)−N(6)	133.6(2)
O(1)−Y(1)−N(3)	81.7(2)	O(3)−Y(2)−N(6)	84.0(2)
O(2)−Y(1)−N(3)	85.6(2)	O(4)−Y(2)−N(6)	84.4(2)
N(1)−Y(1)−N(3)	148.2(2)	N(4)−Y(2)−N(6)	146.9(2)
N(2)−Y(1)−N(3)	82.9(2)	N(5)−Y(2)−N(6)	81.3(2)
Y(1)−Cl(1)−Y(2)	107.19(8)	Y(1)−Cl(2)−Y(2)	107.40(8)
Y(1)−O(1)−C(1)	146.1(5)	Y(2)−O(3)−C(42)	139.6(6)
Y(1)−O(2)−C(15)	136.7(6)	Y(2)−O(4)−C(56)	147.2(5)

The six-coordinate structure of **2** is typical of the majority of complexes reported to date (and several herein) with $O_2{}^RNN'$ ligands and their homologues . The complex possesses approximate C_s symmetry with the pyridine ligand lying *trans* to the pyridyl nitrogen of $O_2{}^{tBu}NN'$. The Sc−donor atom distances are within the expected ranges.[21,22] As is usual, the phenoxy ligand aromatic rings are slightly "bent back" from the pyridine ligand site. This geometric feature, and the fact that the steric bulk of the ring *ortho tert*-butyl substituents is orientated in an axial direction (broadly in line with the Sc−Cl vector), presumably contributes to the need to have an additional sixth ligand occupying the pyridine site in **2**. The NMR data for **2** are fully consistent with the solid state structure. At ambient temperature the pyridine resonances are rather broad, consistent with a dissociative dynamic equilibrium between **2** and a pyridine-free homologue. The NMR data reported in the Experimental Section were recorded at 279 K, at which temperature the pyridine resonances are sharp and all H−H couplings can be clearly resolved.

The scandium centers in dimeric **3** (Figure 2) are also six-coordinate but involve bridging phenoxide oxygens (*not* chlorides). The asymmetric unit of **3**·$2CH_2Cl_2$ contains two half-molecules of $Sc_2(O_2{}^{Me}NN')_2Cl_2$ (lying across crystallographic inversion centers) and two molecules of co-crystallized dichloromethane. No significant differences were observed between the two independent molecules of **3**, and for the purposes of this discussion only that containing Sc(1) will be considered. The structure of compound **3** is somewhat similar to $Sc_2(L_2)(DMSO)_2$ (L = *p*-*tert*-butyloxacalix[3]arene), which also possesses a $Sc_2(\mu\text{-}O)_2$ core with bridging phenoxy linkages.[23] The distances about Sc(1) in **3** are rather similar to those in monomeric **2** with the expected exception of the slightly longer distances to the bridging oxygen atoms in **3**. The NMR spectra of **3** are sharp at room temperature and fully consistent with the solid state structure. In particular there are clear resonances for two inequivalent phenoxymethyl "arms" for the bridging and nonbridging oxygens.

The dimeric congener $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2$ (**4**, Figure 3) possesses bridging chloride ligands rather than dimerizing via the phenoxy oxygens as in **3** (possibly owing to the larger *ortho tert*-butyl ring substituents in the former). In addition, the larger metal accommodates a pyridine molecule at each yttrium, giving seven-coordinate centers. The molecules have approximate C_2 symmetry (rotation axis perpendicular to the $Y_2(\mu\text{-}Cl)_2$ plane). The yttrium centers possess distorted capped trigonal prismatic geometries, the capping atoms being the tripodal amine nitrogens. The prisms are linked by the two μ-Cl atoms, which lie on the mutual edge of the two noncapped faces of the respective prisms. The only other complex containing a $Y_2(\mu\text{-}Cl)_2$ core and seven-coordinate yttrium atoms is $Y_2({}^tBu_2salen)_2(\mu\text{-}Cl)_2(THF)_2$,[24] and the geometry of **4** is similar to this. The bond parameters for **4** are within the previously found ranges.[21,22] Unlike with **2**, no room-temperature broadening of the pyridine resonances was observed for **4**, indicating that no dissociation of the pyridine ligands occurs on the NMR time scale. The NMR spectra of **4** in dichloromethane-d_2 were not entirely consistent with the solid state structure. In Figure 3 the two phenoxy rings of **4** are not equivalent, but in the NMR spectra resonances for only a single C_s symmetric $O_2{}^{tBu}NN'$ ligand environment are seen, although the slight broadening of the resonances assigned to the CH_2Ar protons at 3.30 and 4.16 ppm indicate a fluxional process at room temperature. Indeed, on cooling of the NMR sample, a partial decoalescence of some of the ligand resonances is seen, most notably for

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[21] Allen, F. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 1 and 31.

[22] Fletcher, D. A.; McMeeking, R. F.; Parkin, D. J. *Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

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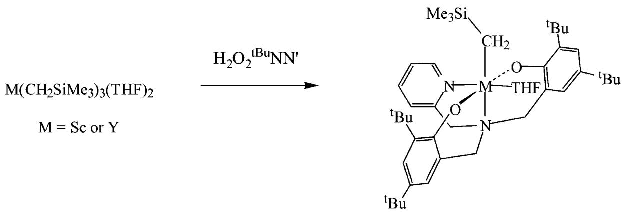
[24] Evans, W. J.; Fujimoto, C. H.; Ziller, J. W. *Chem. Commun.* **1999**, 311.

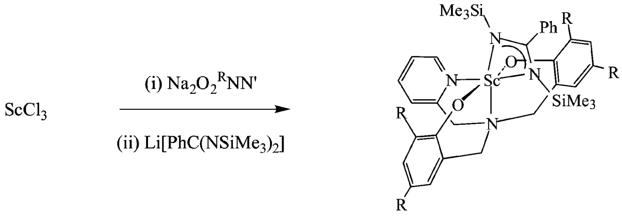
these CH_2Ar proton resonances. However, this fluxional process could not be "frozen out" even at −80 °C, so the room-temperature data are reported here. Assuming that a dimeric structure is maintained in solution, the fluxional process appears to involve aryloxide ring exchange via overall net rotation around the Y(1)···Y(2) vector.



M = Sc (**5**) or Y (**6**)

(1)

Halide substitution reactions of **2** or **4** with a range of lithium or magnesium alkyls or $LiN(SiMe_3)_2$ were unsuccessful. The most promising of these was the reaction of **2** with $LiCH_2SiMe_3$, which appeared to form $Sc(O_2{}^{tBu}NN')(CH_2SiMe_3)(py)$, but this product degraded with further handling/workup and could not be obtained in pure form. However, well-defined alkyls were readily obtained through the protonolysis reactions summarized in eq 1. Thus reaction of $H_2O_2{}^{tBu}NN'$ with $M(CH_2SiMe_3)_3(THF)_2$ in THF (−78 °C) or benzene (7 °C) afforded the six-coordinate compounds $M(O_2{}^{tBu}NN')(CH_2SiMe_3)(THF)$ (M = Sc (**5**) or Y (**6**)) in 63 and 77% yield, respectively. Attempts to recrystallize **6** were problematic, and although this compound is spectroscopically pure, the %C by elemental analysis was repeatedly low. Treatment of $[ScPh_3(THF)_2]$[25] with 1 equiv of $H_2O_2{}^{tBu}NN'$ yielded a complex mixture of products that quickly decomposed in solution even in the absence of light. ^1H NMR NOE experiments conclusively supported the isomers shown in eq 1 (CH_2SiMe_3 *cis* to both pyridyl and THF). In this regard the compounds **5** and **6** are valence isoelectronic with the isolated zirconium cations $[Zr(O_2{}^{tBu}NN')(CH_2Ph)(THF)]^+$ reported by us previously.[7]



R = ^tBu (**7**) or Me (**8**)

(2)

N,N′-Bis(trimethylsilyl)benzamidinate scandium complexes $Sc(O_2{}^RNN')\{PhC(NSiMe_3)_2\}$ (R = ^tBu (**7**) or Me (**8**)) were prepared according to the one-pot reactions shown in eq 2 in ca. 40% recrystallized yields. Direct treatment of $Sc(O_2{}^{tBu}NN')Cl(py)$ (**2**) with $Li[PhC(NSiMe_3)_2]$, although promising on the NMR tube scale, did not scale-up cleanly. Group 3 benzamidinate complexes have been studied in detail by Teuben, Arnold, and others.[26] We have reported the related structurally characterized diamino-diamide complexes $M(N_2NN')\{PhC(NSiMe_3)_2\}$ (M = Sc or Y), which were found to be fluxional (apparent rotation about the $M\cdots C(Ph)N_2$ vector) on the NMR time scale at room temperature.[5]

Compounds **7** and **8** are also fluxional at room temperature on the NMR time scale. Thus the $O_2{}^RNN'$ ligand subspectra indicate apparent molecular C_s symmetry and the two $SiMe_3$ groups of the $PhC(NSiMe_3)_2$ ligands appear as single resonances (integrating as 18 H with respect to those of $O_2{}^RNN'$), which are broad for **7** and sharp for **8**. This is not consistent with the structures proposed in eq 2, which place the $SiMe_3$ groups in different environments. Cooling dichloromethane-d_2 solutions of **7** and **8** causes the fluxional process (apparent rotation about the $M\cdots C(Ph)N_2$ vector that exchanges the $SiMe_3$ groups) to be frozen out. Such fluxional behavior is characteristic of many benzamidinate complexes, and sometimes it can never be frozen out on the NMR time scale.[27] Free energies of activation at the coalescence temperatures T_c ($\Delta G^{\ddagger}{}_{Tc}$) were estimated from the variable-temperature ^1H NMR spectra using standard procedures:[28,29] For **7** ($T_c = 281 \pm 1$ K) $\Delta G^{\ddagger}{}_{281} = 55.1 \pm 0.3$ kJ mol^{-1} and for **8** ($T_c = 210$ K) $\Delta G^{\ddagger}{}_{210} = 41.0 \pm 1.0$ kJ mol^{-1}. Activation energies obtained from coalescence temperature measurements cannot be directly compared, however, because of the $\Delta S^{\ddagger}$ contribution ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$). Thus an analysis of the $SiMe_3$ line widths for **7** at six temperatures in the range 243−263 K yielded exchange rate constants, which were fitted to an Eyring plot,[28] yielding $\Delta H^{\ddagger} = 54.2 \pm 0.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = 6.6 \pm 2.0$ J mol^{-1} K^{-1}. From these data $\Delta G^{\ddagger}{}_{210}$ (i.e., calculated at the T_c for **8**) for **7** was found to be 52.8 ± 0.9 kJ mol^{-1}, some ca. 12 ± 2 kJ mol^{-1} higher than that for **8** ($\Delta G^{\ddagger}{}_{210} = 41.0 \pm 1.0$ kJ mol^{-1}). We attribute the higher $\Delta G^{\ddagger}$ for **7** to the greater steric impedance imposed by the $O_2{}^{tBu}NN'$ ligand *ortho tert*-butyl groups. The small magnitude of $\Delta S^{\ddagger}$ is consistent with a nondissociative fluxional process.

Titanium Bis(dimethylamide), Dichloride, and Dimethyl Compounds. The synthesis and some reactions of the compounds $Ti(O_2{}^RNN')Cl_2$ (R = ^tBu (**9**) or Me (**10**)), $Ti(O_2{}^RNN')(NMe_2)_2$ (R = ^tBu (**11**) or Me (**12**)), and $Ti(O_2{}^RNN')(NMe_2)(S\text{-}4\text{-}C_6H_4Me)$ (**13**) are summarized in Scheme 2.

The most convenient syntheses of the dichloride compounds **9** and **10** are by the sequential addition of MeLi (2 equiv) and then $H_2O_2{}^RNN'$ to $TiCl_4(THF)_2$ in diethyl ether at −40 °C. After crystallization the target compounds are obtained in 65−70% yield. This reaction proceeds through protonolysis of the presumed intermediate $TiMe_2Cl_2(L)_2$ (L = Et_2O or THF)[30] by $H_2O_2{}^RNN'$ (i.e., elimination of methane) A similar method for making **9** starting from $Ti(NMe_2)_2Cl_2$ and $H_2O_2{}^{tBu}NN'$ (i.e., elimination of $HNMe_2$) has also been employed

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[25] Putzer, M. A.; Bartholomew, G. P. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1777.

[26] See for example: Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. Duchateau, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1996**, *15*, 1656. Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197. Edelmann, F. T.; Richter, J. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 157. Hagedorn, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984.

[27] See the following and references therein: Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1982. Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 3616.

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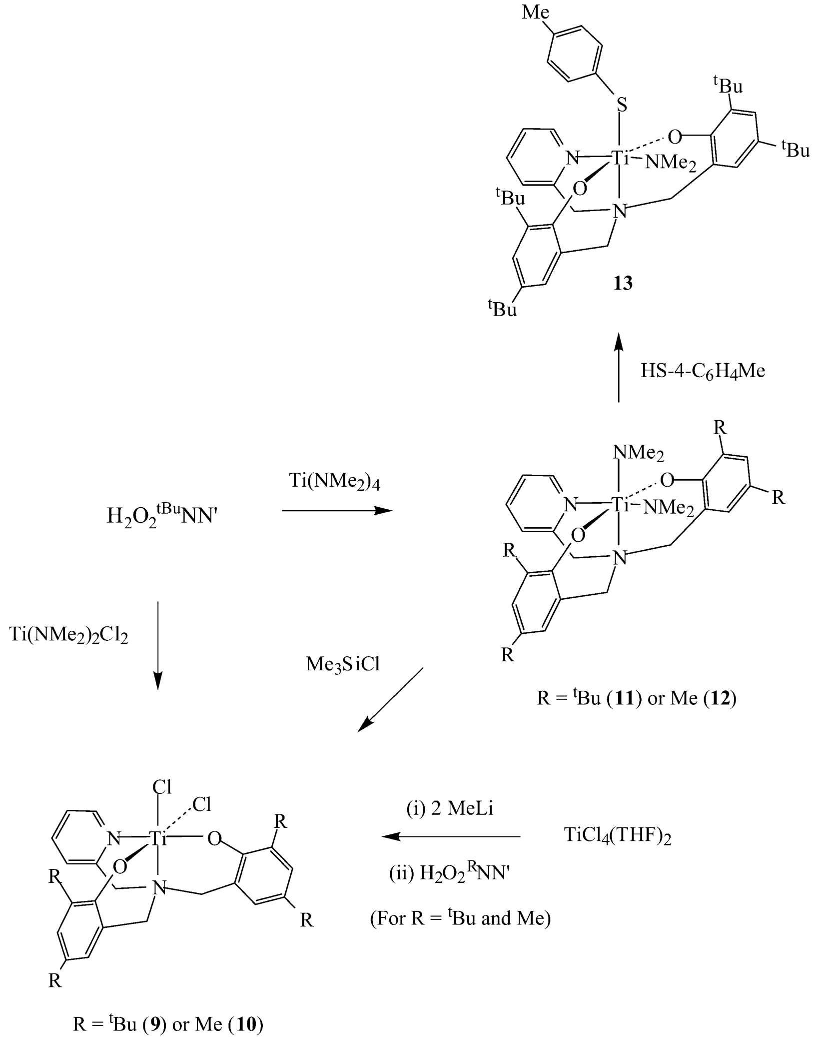
[30] Duncan, D.; Livinghouse, T. *Organometallics* **1999**, *18*, 4421.

Scheme 2. Synthesis and Reactions of Dichloride and Dimethylamide Complexes



(46% isolated yield). It was also shown on an NMR tube scale that reaction of Me_3SiCl (2 equiv) with $Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (**11**) in benzene-d_6 gives **9** and Me_3SiNMe_2 as a side-product after 3 days in quantitative yield. The route to **9** and **10** via $TiMe_2Cl_2(L)_2$ parallels that used by us[7] for the congeners $Zr(O_2{}^{R}NN')Cl_2$ starting from $H_2O_2{}^{R}NN'$ and $Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2$ with the elimination of 2 equiv of $SiMe_4$. Protonolysis methodology also allow the synthesis of the bis(dimethylamide) derivatives **11** and **12** via the smooth reaction of $Ti(NMe_2)_4$ and $H_2O_2{}^{R}NN'$, affording the desired compounds in ca. 80–90% yield. The solid state structures of **9**, **10**, and **11** have been determined and are shown in Figures 4–6; selected distances and angles are summarized in Tables 4–6.

The molecular structures of $Ti(O_2{}^{R}NN')Cl_2$ (R = ^{t}Bu (**9**) or Me (**10**)) are similar, featuring approximately octahedral coordination at titanium and mutually *cis* chloride and phenoxide ligands. The overall symmetry is C_1, and the *cis* arrangement of the phenoxy groups contrasts their arrangement in all of the other structures described herein, but are analogous to that found in the solid state for $Zr(O_2{}^{Me}NN')Cl_2$.[7] The metric parameters for **9** and **10** are within the expected ranges.[21,22] Most of the titanium–donor atom distances in the more sterically crowded **9** are slightly longer than their counterparts in **10**, but this is only a small effect. In both compounds the Ti–Cl bonds *trans* to phenoxide are significantly longer than those *trans* to the tertiary amine nitrogens, consistent with the respective *trans* influences. Interestingly, the solid state structure of $Zr(O_2{}^{tBu}NN')Cl_2$[7] has a *trans* disposition of the phenoxide rings in the solid state. However, the NMR data show that in solution this compound exists as a mixture of *cis* (C_1) and *trans* (C_s) isomers in a 65:35 ratio. $Zr(O_2{}^{Me}NN')Cl_2$ also exists as two isomers in solution but with a *cis*:*trans* ratio of 95:5. The NMR spectra of **9** and **10** are consistent with the solid state structures but show evidence for the presence of a small amount of a second, C_2 symmetric, species in the ratios 92 (C_1):8 and 95:5, respectively. The signals for the two isomers in each case are sharp up to 90 °C in toluene-d_8. This contrasts with the zirconium systems, which are fluxional and undergo intramolecular *cis*/*trans* interconversion at ambient temperature. The activation parameters for the exchange process for $Zr(O_2{}^{tBu}NN')Cl_2$ suggested a very ordered transition state ($\Delta S^{\ddagger} = -102(5)$ J mol^{-1} K^{-1}) consistent with a nondissociative exchange mechanism. The nonfluxional nature of **9** and **10** would be consistent with this since the atomic radius of titanium is smaller than that of zirconium, making nondissociative rearrangement a higher energy process.

The molecular structure of $Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (**11**) shown in Figure 6 shows a *trans* arrangement of the

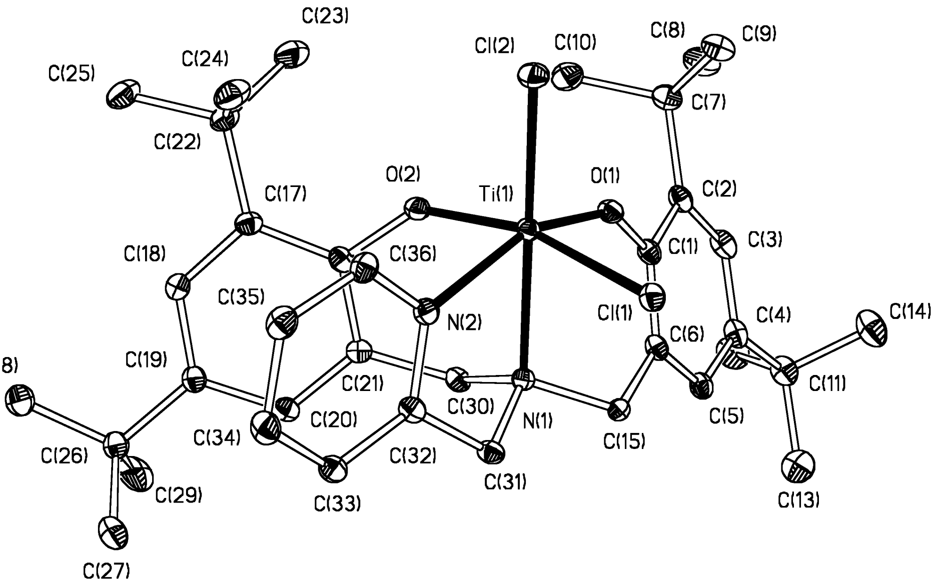


Figure 4. Displacement ellipsoid plot (20% probability) of $Ti(O_2{}^{tBu}NN')Cl_2{\cdot}0.5CH_2Cl_2$ (**9**$\cdot$$0.5CH_2Cl_2$). H atoms and CH_2Cl_2 molecule of crystallization omitted for clarity.

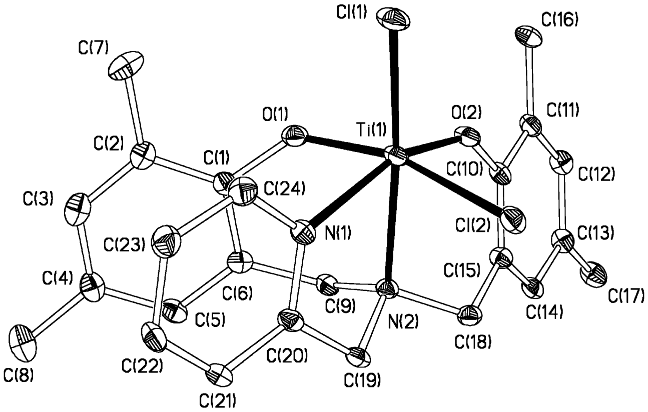
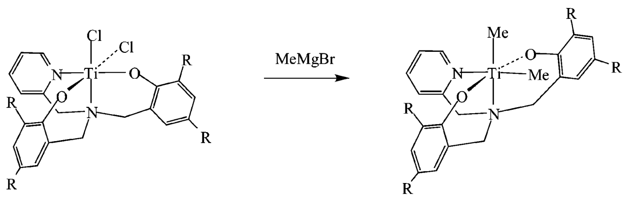


Figure 5. Displacement ellipsoid plot (20% probability) of $Ti(O_2{}^{Me}NN')Cl_2{\cdot}2.5C_6H_6$ (**10**$\cdot$$2.5C_6H_6$). H atoms and C_6H_6 molecules of crystallization omitted for clarity.

phenoxide rings and mutually *cis* NMe_2 ligands. The NMR data for **11** and **12** are entirely consistent and show no evidence for other isomers. Overall the bond lengths and angles for **11** are as expected.[21,22] Interestingly, the difference (0.013(4) Å) between the two $Ti-N_{amide}$ bond lengths is at the margins of statistical significance but suggests that the Ti(1)–N(3) bond is genuinely the shorter of the two. The difference (0.004(4) Å) between the $Ti-N_{pyridyl}$ and $Ti-N_{amine}$ bond lengths is, however, not significant. The sums of the angles subtended at the NMe_2 nitrogens are ca. 360°, showing that these are sp^2 hybridized and formally each able to act as three-electron donors ($\sigma + \pi$) to the metal center. For maximum π donation from the NMe_2 nitrogens to titanium the $2p_\pi$ lone pairs should overlap with orthogonal "t_{2g}" type d_π acceptor orbitals (in Figure 6 these would be the d_{xz} and d_{yz} orbitals if the local z axis is defined as the Ti(1)···N(4) vector). Therefore the dihedral angle C(40)–N(4)–Ti(1)–N(3) should ideally be 0° to achieve maximum $N(p_\pi)-Ti(d_\pi)$ overlap, whereas in **11** this angle is 38.7°. It is likely that steric repulsions between the methyl group of C(39) and the pyridyl *ortho* H atom (bonded to C(36)) prevent the optimum arrangement of the two NMe_2 ligands. The slightly longer Ti(1)–N(4) bond length of Ti(1)–N(3) may be traced to increased steric repulsion in the apical position (between the NMe_2 ligand and the pyridyl *ortho* hydrogen and the phenoxide ring *ortho tert*-butyl groups).

In addition to the reaction of **11** with Me_3SiCl (2 equiv) to yield $Ti(O_2{}^{tBu}NN')Cl_2$ (**9**) several protonolysis reactions were investigated with phenols, thiols, and primary amines. Of those attempted, only the reaction with HS-4-C_6H_4Me yielded a clean product, namely, $Ti(O_2{}^{tBu}NN')(NMe_2)$(S-4-$C_6H_4Me$) (**13**, Scheme 2), which was isolated in 52% yield as a yellow-brown powder. Reaction of **11** with 2 equiv of the thiophenol did not lead to replacement of more than the one NMe_2 ligand. The apical location of the S-4-C_6H_4Me ligand in **13** was established by a ^1H NMR NOE experiment. It is not unreasonable to rationalize the exclusive substitution of the apical NMe_2 ligand on the basis of the structural data, which suggest that this is the more weakly bound NMe_2 ligand and presumably has the more basic nitrogen atom (longest $Ti-NMe_2$ bond and therefore the most polar).



(3)

R = ^tBu (**9**) or Me (**10**)

R = ^tBu (**14**) or Me (**15**)

We were particularly interested in preparing titanium dimethyl derivatives because of their importance as polymerization catalyst precursors. Reaction of $Ti(O_2{}^{R}NN')Cl_2$ (**9**, **10**) with 2 equiv of MeMgBr in benzene or toluene gave modest yields of the corresponding dimethyls $Ti(O_2{}^{R})Me_2$ (R = ^tBu (**14**) or Me (**15**), eq 3). The NMR spectra for the new compounds are consistent with the C_s symmetric structures illustrated and possess two inequivalent Ti-Me ligands. No evidence for alternative C_1 symmetric isomers was found by NMR. Attempts to

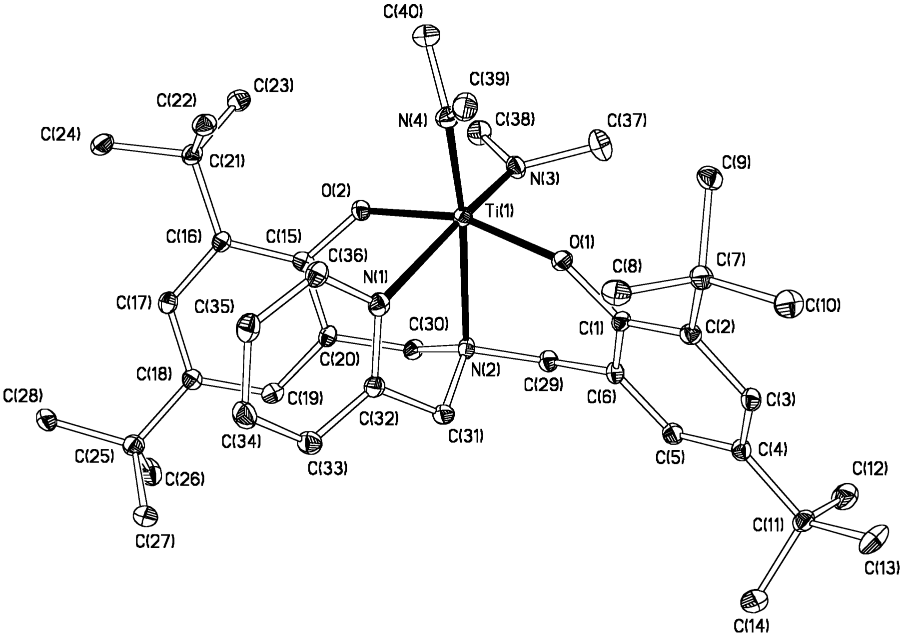


Figure 6. Displacement ellipsoid plot (25% probability) of Ti(O_2^{tBu}NN′)(NMe_2)$_2$ (**11**). H atoms omitted for clarity.

obtain diffraction-quality crystals of either compound were unsuccessful. The structures of well-defined monomethyl cations derived from **14** and **15** are described later in this contribution.

Synthesis and Structures of Imidotitanium Complexes. Over recent years we and others have described the synthesis of a number of classes of imidotitanium complexes and their reactions with unsaturated substrates. Aryloxide-supported group 4 imido derivatives were first prepared by Rothwell and co-workers.[31] We have reported on the structures and bonding of imidotitanium compounds with monodentate aryloxide ligands, focusing on how the nuclearity and coordination number can be fine-tuned by aryloxide O- and imido N-substituents.[32] Of particular relevance to this present contribution is our recent work with calix[4]arene-supported imidotitanium complexes[33] which undergo imido group transfer and/or coupling reactions with CO_2 and other heterocumulenes. We were interested to explore the structures and reactivity of titanium imido complexes supported by O_2^{R}NN′ and a related monoamino-bis(phenoxide) ligand. As a benchmark unsaturated substrate we chose CO_2, which has been shown previously to have a varied reaction chemistry with Ti=NR bonds depending on the identity of the supporting ligand set and the imido N-R substituent itself.[33-35]

tert-Butyl- and aryl-imido titanium compounds can show markedly different reactions with CO_2.[35] Thus the two new compounds Ti(O_2^{tBu}NN′)(NR)(py) (R = ^{t}Bu (**16**) or 2,6-$C_6H_3Me_2$ (**17**)) were prepared from Na_2O_2^{tBu}NN′ and the corresponding Ti(NR)Cl_2(py)$_3$[36] (Scheme 3). Attempts to prepare homologues with the O_2^{Me}NN′ ligand were unsuccessful. The new compounds **16** and **17** were isolated by crystallization from benzene/pentane in 48 and 80% yield, respectively. The NMR spectra were consistent with the six-coordinate C_s symmetric structures shown in Scheme 3. The X-ray molecular structure of **16** confirms the proposed structures (Figure 7), and selected bond lengths and angles are presented in Table 7. A second method for the synthesis of **17** by way of *tert*-butylimide/arylamine exchange was also investigated. Treatment of a solution of **16** in benzene-d_6 with 1 equiv of 2,6-dimethylaniline gave **17** and *tert*-butyaniline in quantitative yield after 6 days at 80 °C. However, due to the efficiency of the direct synthesis of **17** from Na_2O_2^{tBu}NN′ and Ti(N-2,6-$C_6H_3Me_2$)Cl_2(py)$_3$,

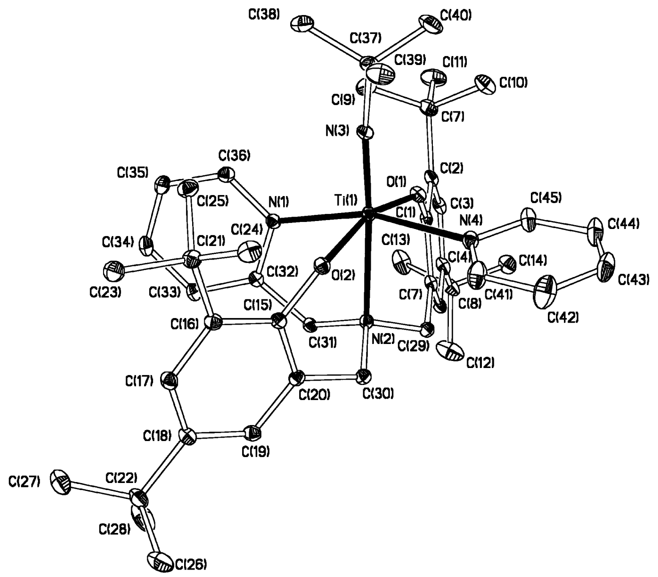


Figure 7. Displacement ellipsoid plot (25% probability) of Ti(O_2^{tBu}NN′)(N^{t}Bu)(py)·2C_6H_6 (**16**·2C_6H_6). H atoms omitted for clarity.

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Scheme 3. Synthesis and Reactions of Imidotitanium Complexes

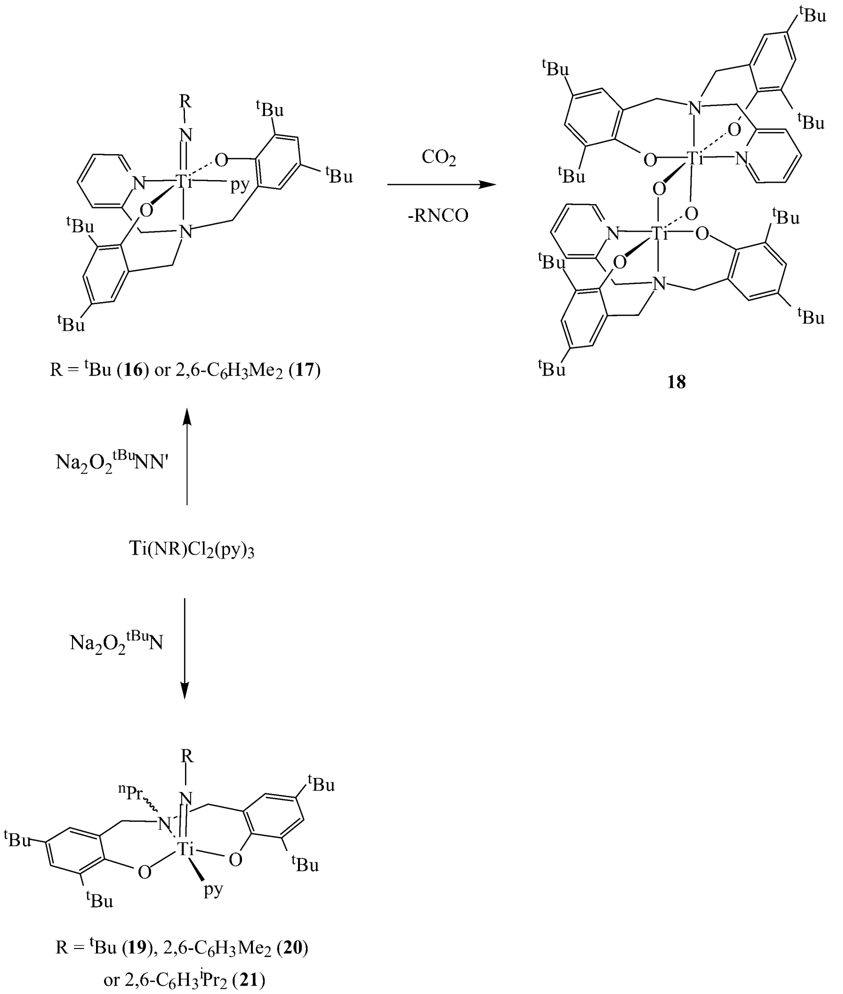

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Ti(O$_2$^{tBu}NN′)Cl$_2$ (9)

Ti(1)−Cl(1)	2.3929(12)	Ti(1)−Cl(2)	2.2840(12)
Ti(1)−O(1)	1.807(3)	Ti(1)−O(2)	1.843(3)
Ti(1)−N(1)	2.260(3)	Ti(1)−N(2)	2.119(3)
Cl(1)−Ti(1)−Cl(2)	90.96(4)	Cl(1)−Ti(1)−N(1)	85.15(9)
Cl(2)−Ti(1)−N(1)	174.51(9)	Cl(1)−Ti(1)−N(2)	80.23(9)
Cl(2)−Ti(1)−N(2)	99.8(1)	N(1)−Ti(1)−N(2)	75.75(12)
Cl(1)−Ti(1)−O(1)	95.9(1)	Cl(2)−Ti(1)−O(1)	101.59(9)
N(1)−Ti(1)−O(1)	82.71(12)	N(2)−Ti(1)−O(1)	158.34(13)
Cl(1)−Ti(1)−O(2)	162.4(1)	Cl(2)−Ti(1)−O(2)	96.59(9)
N(1)−Ti(1)−O(2)	86.11(12)	N(2)−Ti(1)−O(2)	82.78(13)
Ti(1)−O(1)−C(1)	143.2(2)	Ti(1)−O(2)−C(15)	136.3(2)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Ti(O$_2$^{Me}NN′)Cl$_2$ (10)

Ti(1)−Cl(1)	2.306(2)	Ti(1)−Cl(2)	2.372(2)
Ti(1)−N(1)	2.212(5)	Ti(1)−N(2)	2.277(5)
Ti(1)−O(1)	1.844(4)	Ti(1)−O(2)	1.812(4)
Cl(1)−Ti(1)−Cl(2)	92.59(8)	Cl(1)−Ti(1)−N(1)	95.8(1)
Cl(2)−Ti(1)−N(1)	82.7(1)	Cl(1)−Ti(1)−N(2)	171.4(1)
Cl(2)−Ti(1)−N(2)	85.6(1)	N(1)−Ti(1)−N(2)	75.7(2)
Cl(1)−Ti(1)−O(1)	94.8(1)	Cl(2)−Ti(1)−O(1)	163.3(1)
N(1)−Ti(1)−O(1)	81.6(2)	N(2)−Ti(1)−O(1)	84.9(2)
Cl(1)−Ti(1)−O(2)	105.0(1)	Cl(2)−Ti(1)−O(2)	94.2(1)
N(1)−Ti(1)−O(2)	159.2(2)	N(2)−Ti(1)−O(2)	83.5(2)
O(1)−Ti(1)−O(2)	98.3(2)	Ti(1)−N(1)−C(20)	116.8(4)
Ti(1)−O(1)−C(1)	133.8(4)	Ti(1)−O(2)−C(10)	142.5(4)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Ti(O$_2$^{tBu}NN′)(NMe$_2$)$_2$ (11)

Ti(1)−O(1)	1.909(2)	Ti(1)−O(2)	1.927(2)
Ti(1)−N(1)	2.338(3)	Ti(1)−N(2)	2.342 (3)
Ti(1)−N(3)	1.927(3)	Ti(1)−N(4)	1.940(3)
N(1)−Ti(1)−N(2)	72.5(1)	N(1)−Ti(1)−N(3)	165.84(11)
N(2)−Ti(1)−N(3)	95.91(11)	N(1)−Ti(1)−N(4)	92.52(12)
N(2)−Ti(1)−N(4)	164.43(11)	N(3)−Ti(1)−N(4)	99.53(13)
N(1)−Ti(1)−O(1)	88.7(1)	N(2)−Ti(1)−O(1)	79.20(9)
N(3)−Ti(1)−O(1)	97.14(11)	N(4)−Ti(1)−O(1)	96.81(11)
N(1)−Ti(1)−O(2)	80.6(1)	N(2)−Ti(1)−O(2)	84.0(1)
N(3)−Ti(1)−O(2)	90.37(11)	N(4)−Ti(1)−O(2)	97.79(11)
O(1)−Ti(1)−O(2)	162.2(1)	Ti(1)−O(1)−C(1)	143.2(2)
Ti(1)−O(2)−C(15)	136.3(2)		

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Ti(O$_2$^{tBu}NN′)(N^{t}Bu)(py) (16)

Ti(1)−O(1)	1.965(2)	Ti(1)−O(2)	1.976(2)
Ti(1)−N(1)	2.230(2)	Ti(1)−N(2)	2.442(2)
Ti(1)−N(3)	1.719(2)	Ti(1)−N(4)	2.254 (2)
N(1)−Ti(1)−N(2)	73.11(9)	N(1)−Ti(1)−N(3)	102.44(11)
N(2)−Ti(1)−N(3)	175.43(11)	N(1)−Ti(1)−N(4)	162.6(1)
N(2)−Ti(1)−N(4)	90.12(9)	N(3)−Ti(1)−N(4)	94.39(11)
N(1)−Ti(1)−O(1)	93.40(9)	N(2)−Ti(1)−O(1)	80.15(8)
N(3)−Ti(1)−O(1)	99.30(11)	N(4)−Ti(1)−O(1)	88.0(1)
N(1)−Ti(1)−O(2)	85.92(9)	N(2)−Ti(1)−O(2)	81.89(8)
N(3)−Ti(1)−O(2)	98.98(11)	N(4)−Ti(1)−O(2)	87.3(1)
O(1)−Ti(1)−O(2)	161.41(9)	Ti(1)−N(3)−C(37)	171.5(2)
Ti(1)−O(1)−C(1)	139.9(2)	Ti(1)−O(2)−C(15)	134.5(2)

this exchange route was not repeated on a preparative scale.

The molecular structure of **16** features bond lengths and angles within the usual ranges.[21,22] The observation that the N(3)−Ti(1)−donor-atom angles are all greater than 95−100° is typical for six-coordinate imido complexes.[21,22,36] The titanium to pyridyl (N(1)) and pyridine

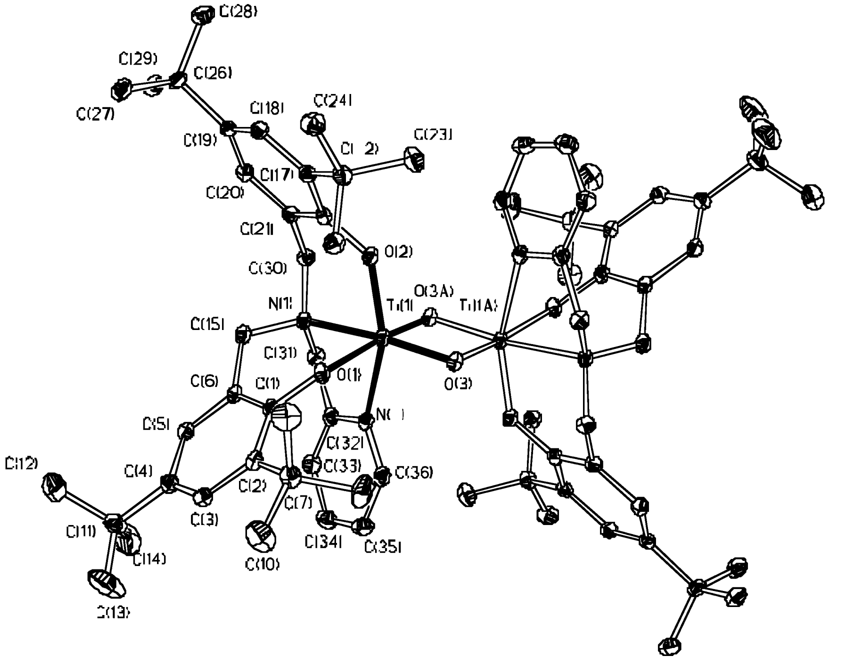

Figure 8. Displacement ellipsoid plot (35% probability) of $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2\cdot3CH_2Cl_2$ (**18**·$3CH_2Cl_2$). H atoms and CH_2Cl_2 molecules of crystallization omitted for clarity.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2$ (18)

Ti(1)−O(1)	1.921(2)	Ti(1)−O(2)	1.894(2)
Ti(1)−N(1)	2.299(3)	Ti(1)−N(2)	2.231(3)
Ti(1)−O(3)	1.776(2)	Ti(1)−O(3A)	1.965(2)
O(3)−Ti(1)−O(3A)	82.91(11)	Ti(1)−O(3)−Ti(1A)	97.09(11)
Ti(1)−O(1)−C(1)	134.0(2)	Ti(1)−O(2)−C(16)	134.9(2)
O(1)−Ti(1)−O(2)	94.2(1)	O(1)−Ti(1)−O(3)	105.3(1)
O(2)−Ti(1)−O(3)	106.51(11)	O(1)−Ti(1)−O(3A)	163.9(1)
O(2)−Ti(1)−O(3A)	96.7(1)	N(1)−Ti(1)−N(2)	73.1(1)
O(1)−Ti(1)−N(1)	85.3(1)	O(2)−Ti(1)−N(1)	86.1(1)
O(3)−Ti(1)−N(1)	162.6(1)	O(3A)−Ti(1)−N(1)	83.68(9)
O(1)−Ti(1)−N(2)	81.9(1)	O(2)−Ti(1)−N(2)	159.0(1)
O(3)−Ti(1)−N(2)	94.4(1)	O(3A)−Ti(1)−N(2)	83.6(1)

(N(4)) distances are rather similar, but the *trans* (to N^tBu) coordinated amino nitrogen N(2) has a much longer bond length to titanium, consistent with the well-known *trans* influence of imido ligands.[37] The imido ligand in **16** acts as a four-electron donor (1 σ and 2 π orbital interactions) being essentially sp-hybridized (Ti(1)−N(3)−C(37) = 171.5(2)°). The six-coordination of **16** is rather unusual in the sense that all previously reported bis(aryloxide) imidotitanium compounds have been either five- or four-coordinate, but presumably this is a simple consequence of the chelating tetradentate nature of $O_2{}^{tBu}NN'$.

The reactions of $Ti(NR)(O_2{}^{tBu}NN')(py)$ (**16** or **17**) with CO_2 (1 atm) were assessed by NMR tube scale experiments. In each case the corresponding isocyanate RNCO was formed quantitatively within 1 h along with the μ-oxo-bridged dimer $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2$ (**18**) and free pyridine. The compound **18** was most easily made on a preparative scale by the carefully controlled hydrolysis of **16**. The X-ray molecular structure of **18** is shown in Figure 8, and selected bond lengths and angles are listed in Table 8. The NMR data for **18** are consistent with the solid state structure. On the basis of the literature in this area we propose that the formation of **18** proceeds via CO_2 cycloaddition to the Ti=NR linkages of **16** or **17**, yielding N,O-bound carbamate products of the type $Ti(O_2{}^{tBu}NN')\{NRC(O)O\}$ (not observed). These then subsequently extrude (by cycloreversion) RNCO.

In general terms the $Ti_2(\mu\text{-}O)_2$ core of **18** (Figure 8) is well-established in the structural chemistry of titanium.[21,22] Notably, however, there is a pronounced asymmetry as manifested by rather different Ti−O distances of 1.776(2) (*trans* to tertiary amine N) and 1.965(2) Å (*trans* to aryloxide O), which may be attributed in part to the differing *trans* labilizing ability of the respective donors opposite the Ti−O bonds. The difference (ΔTi−O = 0.189(4) Å) between the Ti−O bond distances is, however, much larger than that between the two Ti−Cl distances in the monomeric dichlorides **9** (ΔTi−Cl = 0.109(2) Å) and **10** (ΔTi−Cl = 0.066(4) Å), which also have either an aryloxide O or tertiary amine N *trans* to the individual Ti−Cl bonds. Therefore the extreme differential lengthening of the Ti−O bonds in **18** is probably also due to steric repulsion between the neighboring $O_2{}^{tBu}NN'$ ligands of the two Ti atoms.

Apart from those associated with the $Ti_2(\mu\text{-}O)_2$ unit, the distances and angles around the Ti centers are within the expected ranges.[21,22] Note, however, that the overall dimeric structure of **18** is rather different from those of $Sc_2(O_2{}^{Me}NN')_2Cl_2$ (**3**, Figure 2) and $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2$ (**4**, Figure 3). In both **3** and **4** the aryloxide donors within each $O_2{}^{R}NN'$ ligand adopt a mutually *trans* disposition, whereas in **18** they are mutually *cis*, just as in the dichlorides **9** and **10**. It is possible that in **18** the *cis* arrangement is chosen to reduce the degree of repulsion between the neighboring $O_2{}^{tBu}NN'$ ligands. In **3** the $O_2{}^{Me}NN'$ ligands do not bear the bulky *ortho tert*-butyl groups, and in **4** there is a greater separation of the neighboring $O_2{}^{tBu}NN'$ ligands due to the longer Y−Cl bonds. Other factors may also be important in setting the overall geometry of **18** and the other two dimers, but those highlighted here are

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[37] See the following and references therein: Kaltsoyannis, N.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1999**, 781.

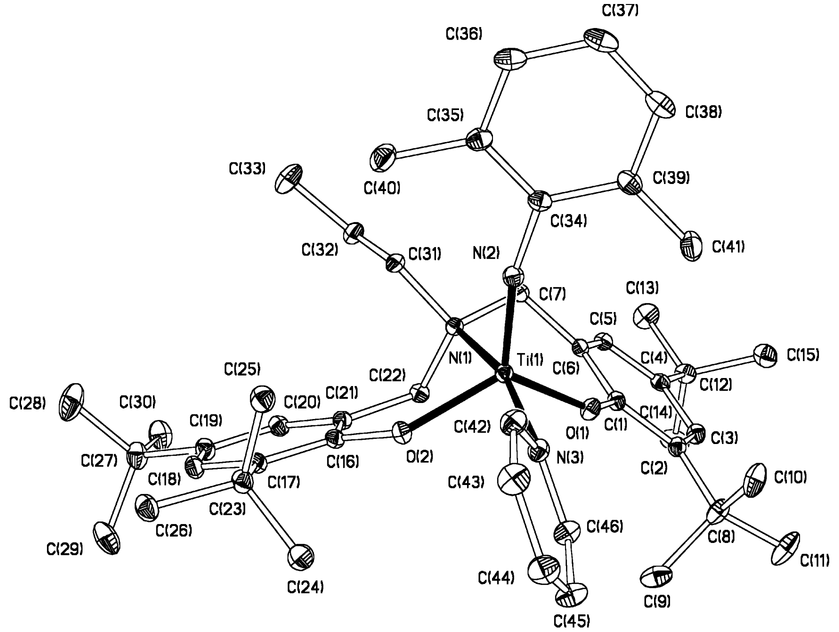


Figure 9. Displacement ellipsoid plot (25% probability) of $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)\cdot 0.5C_6H_6$ (**20**$\cdot 0.5C_6H_6$). H atoms and benzene molecule of crystallization omitted for clarity.

undoubtedly important. The three compounds **3**, **4**, and **18** exemplify the subtle structural variations that can be anticipated for $O_2{}^{R}NN'$ and related ligands.

We now return again to the reactions with CO_2. Although cycloreversion reactions of first-formed carbamates to form oxotitanium compounds and isocyanates are well-established in the reactions of imidotitanium compounds with CO_2,[33–35] it is rather unusual not to observe the initial formation of a carbamate intermediate, especially for aryl imides. We speculated that the tetradentate nature of $O_2{}^{tBu}NN'$ might lead to a rather crowded six-coordinate carbamate intermediate and that steric repulsions might promote the extrusion/cycloreversion reaction. We therefore targeted imidotitanium complexes of the tridentate ligand $O_2{}^{tBu}N$ (Chart 1) as shown in Scheme 3.

Reaction of $Na_2O_2{}^{tBu}N$ with $Ti(NR)Cl_2(py)_3$ ($R = {}^tBu$, $2,6\text{-}C_6H_3Me_2$ or $2,6\text{-}C_6H_3{}^iPr_2$) afforded the corresponding five-coordinate complexes $Ti(NR)(O_2{}^{tBu}N)(py)$ (**19**, **20**, and **21**) in 3%, 45%, and 21% yields, respectively. Due to the very low yield of $Ti(N^tBu)(O_2{}^{tBu}N)(py)$ (**19**) and difficulties in obtaining an analytically pure sample, this compound was characterized by ^1H NMR spectroscopy only. All three compounds exist as a mixture of two isomers in solution (ratios between the isomers are between 3:2 and 3:1). Both isomers have overall C_s symmetry on the NMR time scale, with pyridine and $O_2{}^{tBu}NN'$ ligands present in a 1:1 ratio. In no case was it possible to separate the two isomers by fractional crystallization on the bulk scale. The ratio of the isomers does not change with time or temperature. Nonetheless for both $Ti(N\text{-}2,6\text{-}C_6H_3Me_2)(O_2{}^{tBu}N)(py)$ (**20**) and $Ti(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(O_2{}^{tBu}N)(py)$ (**21**) we were able to grow a small number of diffraction-quality crystals, and the molecular structures and selected bond lengths and angles are shown in Figures 9 and 10 and in Tables 9 and 10.

Molecules of both **20** and **21** possess approximately trigonal bipyramidal titanium centers. The imido N and aryloxide O atoms define the equatorial plane, and the $O_2{}^{tBu}N$ tertiary amine N and pyridine N atoms occupying the axial positions. In general terms this geometry is typical of five-coordinate imido-titanium (and -zirconium) bis(aryloxide) complexes.[31] The bond distances and angles at the two metal centers are unexceptional for this class of compound.[21,22] The $Ti-N_{amine}$ and Ti−O distances are all shorter for **20** and **21** in comparison with those for six-coordinate $Ti(O_2{}^{tBu}NN')(N^tBu)(py)$ (**16**), whereas the $Ti{=}N_{imide}$ distances are longer by 0.016(3) and 0.003(3) Å, respectively. Only the first bond length difference is statistically significant, but in general one should expect shorter $Ti{=}N_{imide}$ distances for *tert*-butyl imido than for aryl-imido ligands.[37] It is also usually found that *tert*-butyl imido ligands have a greater bond lengthening effect on the other ligands present. Notwithstanding these specific imido ligand effects, the increased coordination number for **16** should lead to a general increase in metal−ligand bond lengths as compared to **20** and **21**.

A more detailed comparison of the molecular structures of **20** and **21** shows that they differ significantly in the conformations of the six-membered chelate rings. The overall effect is to invert the geometry at the $O_2{}^{tBu}N$ amino nitrogen N(1) such that the *n*-propyl substituent is *syn* with respect to $Ti{=}N_{imide}$ in **20** and *anti* with respect to $Ti{=}N_{imide}$ in **21**. We believe that these two differing conformations correspond to the two isomers present in solution and that by good fortune we have obtained the complimentary isomers in the solid state. The two different conformations lead to rather different distances and angles at the two Ti centers. In particular, the Ti−N distances for **20** are all longer than those in **21** despite the presence of the more sterically demanding imido N-substituent in the latter compound. In addition, the two Ti−O distances in **20** are very different (ΔTi−O = 0.026(2) Å), whereas in **21** they are experimentally identical (ΔTi−O = 0.002(2) Å). The two aryloxide rings in **21** are related by a molecular plane of symmetry, whereas in **20** they are not. This difference

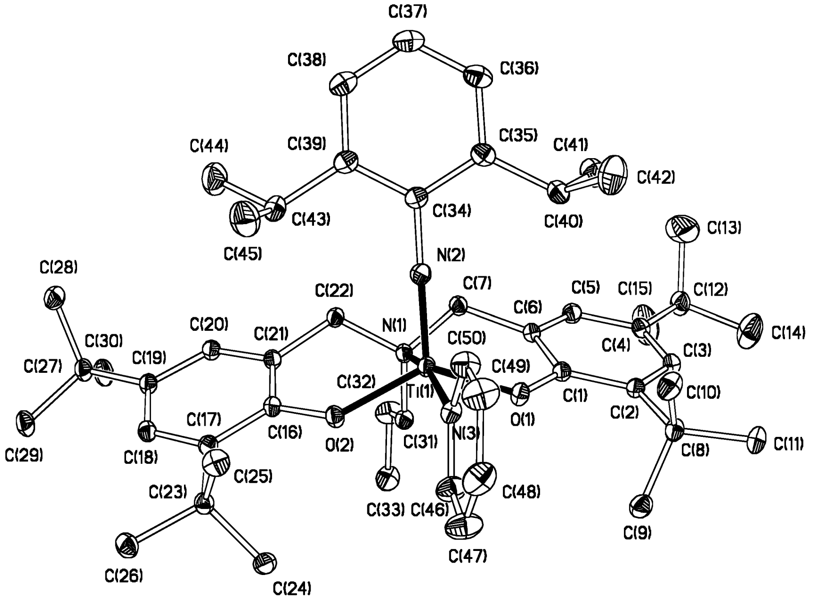


Figure 10. Displacement ellipsoid plot (25% probability) of $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(py)$ (**21**). H atoms omitted for clarity.

Table 9. Selected Bond Lengths (Å) and Angles (deg) for $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)$ (20)

Ti(1)−N(1)	2.2267(15)	Ti(1)−O(1)	1.8862(12)
Ti(1)−N(2)	1.7349(15)	Ti(1)−O(2)	1.9118(12)
Ti(1)−N(3)	2.2247(16)		
O(1)−Ti(1)−O(2)	121.19(6)	N(1)−Ti(1)−N(2)	96.14(6)
O(1)−Ti(1)−N(1)	85.34(5)	O(1)−Ti(1)−N(3)	96.16(5)
O(2)−Ti(1)−N(1)	83.87(5)	O(2)−Ti(1)−N(3)	84.13(5)
O(1)−Ti(1)−N(2)	118.58(6)	N(1)−Ti(1)−N(3)	166.17(6)
O(2)−Ti(1)−N(2)	119.99(6)	N(2)−Ti(1)−N(3)	94.66(6)

Table 10. Selected Bond Lengths (Å) and Angles (deg) for $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(py)$ (21)

Ti(1)−N(1)	2.2199(17)	Ti(1)−O(1)	1.8961(14)
Ti(1)−N(2)	1.7218(18)	Ti(1)−O(2)	1.8984(14)
Ti(1)−N(3)	2.2054(17)		
O(1)−Ti(1)−O(2)	131.63(7)	N(1)−Ti(1)−N(2)	96.66(7)
O(1)−Ti(1)−N(1)	83.65(6)	O(1)−Ti(1)−N(3)	91.63(6)
O(2)−Ti(1)−N(1)	82.99(6)	O(2)−Ti(1)−N(3)	90.32(6)
O(1)−Ti(1)−N(2)	113.31(7)	N(1)−Ti(1)−N(3)	165.85(6)
O(2)−Ti(1)−N(2)	114.30(7)	N(2)−Ti(1)−N(3)	97.46(8)

is not evident in solution on the NMR time scales as stated above.

As mentioned, we prepared the compounds **19**−**21** in an attempt to control the cycloaddition/cycloreversion reactions of CO_2 at the Ti=NR multiple bonds. Regrettably, reaction of either **20** or **21** with CO_2 gave rather complex mixtures, which could not be identified. Thus there is inherently rather different reactivity between the systems supported by the tri- and tetradentate ligands $O_2{}^{tBu}N$ and $O_2{}^{tBu}NN'$ and also between these and the O_4-donor calixarene systems.

Polymerization Studies and Formation of Titanium Monomethyl Cations Supported by $O_2{}^{R}NN'$ Ligands. As mentioned, Kol and co-workers have shown that group 4 dibenzyl compounds supported by diamine-bis(phenoxide) and related ligands can be precatalysts for the polymerization (in some instances living) of 1-hexene.[8−14] The activity depends critically on the metal (titanium or zirconium) and the pendant group ("L") of the $(L)CH_2N(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2R_2)_2$ ligand. In our previous evaluation[7] of ethylene polymerization by the zirconium precatalysts $[Zr(O_2{}^{R}NN')X_2]$ (R = ^{t}Bu or Me; X = Cl, Me, or CH_2Ph) we found that activation with either MAO or $B(Ar^F)_3$ gave very poorly active catalysts. This was rationalized in terms of the unavoidable dilution effect when moving from a neat liquid monomer as the polymerization medium (as used in Kol's work) to toluene and a gaseous monomer. Indeed, it has been shown that the 1-hexene polymerization activity of the $Zr(O_2{}^{R}NN')X_2/B(Ar^F)_3$ catalyst system decreases from 5700 g $mmol^{-1}$ h^{-1} in neat 1-hexene to 650 g $mmol^{-1}$ h^{-1} on dilution to 30% 1-hexene in heptane.[11]

We evaluated the ethylene polymerization activity of the six compounds $Ti(O_2{}^{R}NN')X_2$ (R = ^{t}Bu or Me; X = Cl, NMe_2, or Me) in the presence of MAO cocatalyst (Ti:Al ratio = 1:1500; toluene solvent; 5 bar ethylene). Very low polymerization activities of between 0.9 and 8.9 g $mmol^{-1}$ h^{-1} bar^{-1} were recorded. Under identical conditions, Cp_2ZrCl_2 afforded an activity of 1480 g $mmol^{-1}$ h^{-1} bar^{-1}. The activities for the $O_2{}^{Me}NN'$-supported systems (**12**, 7.8; **10**, 8.9; **15**, 4.8 g $mmol^{-1}$ h^{-1} bar^{-1}) were superior to those of the $O_2{}^{tBu}NN'$-supported homologues (**11**, 2.3; **9**, 0.9; **14**, 1.8 g $mmol^{-1}$ h^{-1} bar^{-1}). Molecular weight distributions were broad, multimodal, and indicative of the formation of several catalytically active species. Even more disappointing was the absence of any activity at all for the dimethyl compounds $Ti(O_2{}^{R}NN')Me_2$ (R = ^{t}Bu (**14**) or Me (**15**)) when activated by $B(Ar^F)_3$, $[CPh_3][B(Ar^F)_4]$, or $[NHMe_2Ph][B(Ar^F)_4]$ in the presence of Al^iBu_3. This behavior parallels that of the zirconium compounds.[7]

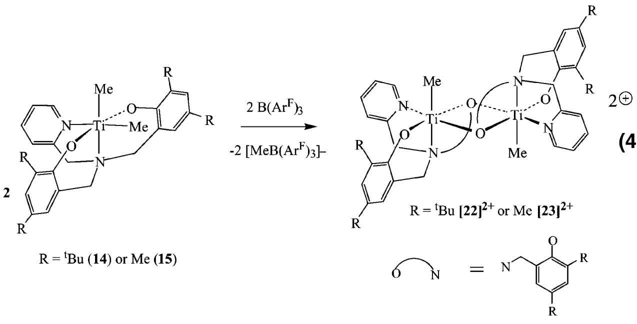
To compare with Kol's work on the $B(Ar^F)_3$-activated systems $M\{(L)CH_2N(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2{}^tBu_2)_2\}R_2$ (M = Ti or Zr, R = alkyl), we evaluated the polymerization of 1-hexene by the catalyst system $Ti(O_2{}^{tBu}NN')Me_2/B(Ar^F)_3$. The polymerization was very sluggish, even in neat 1-hexene, and an activity of only 0.50 g $mmol^{-1}$ h^{-1} was recorded. GPC analysis of the atactic poly(1-hexene) gave M_w = 60 400, M_n = 24 600, and M_w/M_n = 2.5. The slightly high polydispersity index may be attributed to a small high M_w "tail" for the polymer (confirmed by a differential pressure chromatogram), perhaps indicative of a second catalytically active species present in the mixture. Thus **14** provides a homogeneous and predominantly single-site polymerization catalyst with $B(Ar^F)_3$. The low polymerization activity is entirely consistent with previous reports that polymerization by titanium precatalysts $Ti\{(L)CH_2N(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2{}^tBu_2)_2\}(CH_2Ph)_2$ decreases with increasing donor ability of the "L" moiety and that activities for titanium are orders of magnitude lower than those for zirconium. Thus for "L" = CH_2NMe_2,[8] CH_2OMe,[9] or THF,[14] activities in the range 12−30 g $mmol^{-1}$ h^{-1} were reported, but for "L" = furanyl (a less good Lewis base)[13] an activity of 200 g $mmol^{-1}$ h^{-1} was found. For the corresponding zirconium systems,[11] the 1-hexene polymerization activities for "L" = CH_2NMe_2 and 2-pyridyl were 21 000 and 5700 g $mmol^{-1}$ h^{-1}.

We were interested in characterizing the monomethyl cation formed from $Ti(O_2{}^{tBu}NN')Me_2$ (**14**) and $B(Ar^F)_3$. In this context we note that Kol recently reported that the C_s symmetric monobenzyl cation $[Zr(O^{tBu}{}_2NN^*)(CH_2Ph)]^+$ ($H_2O_2{}^{tBu}NN^*$ = $Me_2NCH_2CH_2N(2\text{-}HO\text{-}3,5\text{-}C_6H_2{}^tBu_2)_2$) is formed from $Zr(O^{tBu}{}_2NN^*)(CH_2Ph)_2$ on treatment with $B(Ar^F)_3$.[12] NMR characterization (chlorobenzene-d_5, −35 °C) showed the presence of a noncoordinated $[PhCH_2B(Ar^F)_3]^-$ anion and established that the NMe_2 donor and remaining benzyl group are coordinated *cis* to each other in the proposed five-coordinate cation. This is consistent with our results[7] for the C_s symmetric THF adducts $[Zr(O^R{}_2NN')(CH_2Ph)(THF)]^+$ (R = Me or ${}^tBu$; isolated and fully characterized as their $[PhCH_2B(Ar^F)_3]^-$ salts), which also have the CH_2Ph ligand *cis* to the pyridyl donor.

Reaction of $Ti(O_2{}^{tBu}NN')Me_2$ (**14**) with $B(Ar^F)_3$ in dichloromethane at −78 °C followed by addition of hexanes at 0 °C afforded a red powder (**22**-$[MeB(Ar^F)_3]$). The elemental analysis was consistent with the composition "$[Ti(O_2{}^{tBu}NN')Me]\cdot[MeB(Ar^F)_3]\cdot0.15(CH_2Cl_2)$". The ambient-temperature ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra of the compound in dichloromethane-d_2 showed a noncoordinated $[MeB(Ar^F)_3]^-$ anion,[38] a Ti-Me ligand, and resonances consistent with a C_s symmetric cation (i.e., equivalent $OC_6H_2{}^tBu_2$ rings; one pair of mutually coupled doublets for the NCH_2Ar H atoms and a singlet for the CH_2pyridyl H atoms). Surprisingly, the putative five-coordinate monomethyl cation is stable for several hours in dichloromethane-d_2 at ambient temperature. Furthermore, when ethylene was admitted to the evacuated headspace of an NMR tube sample, no evidence for enchainment was noted before the sample degraded in essentially the same manner as when no ethylene was present. A further NMR tube experiment between **14** and $[CPh_3][B(Ar^F)_4]$ in dichloromethane-d_2 led to an identical titanium-containing cation (along with the expected side-product $MeCPh_3$), confirming that the $[MeB(Ar^F)_3]^-$ anion has no significant effect.

Cooling an NMR sample of "$[Ti(O_2{}^{tBu}NN')Me]\cdot[MeB(Ar^F)_3]$" (**22**-$[MeB(Ar^F)_3]$) in dichloromethane-$d_2$ (^1H frequency 500 MHz) led first to broadening and then subsequently (below 213 K) to decoalescence of most of the methylene and $OC_6H_2{}^tBu_2$ moiety H atom resonances. The H atom resonances for the pyridyl and Ti-Me groups were virtually unchanged on cooling, as was the methyl group resonance of the $[MeB(Ar^F)_3]^-$ anion. At 183 K the ^1H and $^{13}C\{^1H\}$ spectra conclusively show C_1 symmetry; the ^{19}F NMR spectrum at this temperature was still consistent with a noncoordinated $[MeB(Ar^F)_3]^-$ anion.

NMR tube experiments between $Ti(O_2{}^{Me}NN')Me_2$ (**15**) and either $B(Ar^F)_3$ or $[CPh_3][B(Ar^F)_4]$ in dichloromethane-d_2 afforded an analogous monomethyl titanium cation, "$[Ti(O_2{}^{Me}NN')Me]^+$", along with noncoordinated $[MeB(Ar^F)_3]^-$ or $[B(Ar^F)_4]^-$ anions. The spectra for the cationic species were sharp at room temperature, fully consistent with C_1 symmetry and analogous to those of "$[Ti(O_2{}^{tBu}NN')Me]^+$" at 183 K. Attempts to isolate salts of "$[Ti(O_2{}^{Me}NN')Me]^+$" on a preparative scale were unsuccessful.



(4)

Two most likely explanations for the NMR data for "$[Ti(O_2{}^RNN')Me]^+$" can be advanced. The first is that these are five-coordinate monomeric cations with *cis* coordinated aryloxide moieties in the ground state (i.e., rather like the dichlorides $Ti(O_2{}^RNN')Cl_2$ but with one ligand removed) and which are highly fluxional for R = ^{t}Bu but rigid on the NMR time scale for R = Me. The second is that they are dimeric as proposed in eq 4, with titanium centers bridged via phenoxide O atoms just as for the isoelectronic and structurally characterized scandium complex $Sc_2(O_2{}^{Me}NN')_2Cl_2$ (**3**, Figure 2). We favor the second interpretation since it accounts for the more fluxional nature of $[Ti_2(O_2{}^{tBu}NN)_2Me_2]^{2+}$ (more sterically crowded O donors) and is consistent with the clear desire of all seven of the structurally characterized $O_2{}^RNN'$compounds of Sc or Ti reported herein to seek six-coordination.

Our interpretation of the NMR data is not necessarily inconsistent with Kol's report that $[Zr(O^{tBu}{}_2NN^*)(CH_2Ph)]^+$ and related zirconium monobenzyl cations exist as five-coordinate monomeric cations since there is a likelihood that these could be stabilized by additional phenyl ring *ipso* carbon (partial η^2) coordination. On the other hand, the lowest temperature at which Kol's data could be recorded in chlorobenzene-d_5 was −35 °C, and in principle a dimeric species of the type $[Zr_2(O_2{}^{tBu}NN^*)_2(CH_2Ph)_2]^{2+}$ could still be in fast exchange on the NMR time scale at this temperature.

However, regardless of the nature of the first-formed initiating benzyl cation, after the first enchainment of monomer it may be possible that the subsequent propagating species are dimeric in nature.[39] Further work will be needed to address this question and the possible implications with regards to[8,9,11,14] (i) why titanium-based systems based on the ligands $O_2{}^{tBu}NN'$ and $O_2{}^{tBu}NN^*$ and their homologues are less effective polymerization catalysts than their zirconium congeners; (ii) why

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[38] Horton, A. D. *Organometallics* **1996**, *15*, 2675.

[39] Said, M.; Hughes, D. L.; Bochmann, M. *Dalton Trans.* **2004**, 359.

polymerization activities are higher for less effective Lewis base donors; (iii) the long lifetime and living nature of such catalyst systems if their resting states are in fact moderately stable six-coordinate dimers.

Conclusions

The previously reported $O_2{}^RNN'$ ligand provides versatile support for a range of organometallic and coordination complexes of scandium, yttrium, and titanium. Compounds may be prepared via protonolysis or salt elimination methods. The $O_2{}^RNN'$ ligands have an overwhelming tendency to enforce six-coordination (and also higher for the larger Y), resulting in the formation of dimeric species where necessary to achieve this. The steric protection provided by the phenoxide ring *ortho tert*-butyl groups of $O_2{}^{tBu}NN'$ is inadequate for blocking dimerization through the phenoxy O atoms for larger or more Lewis acidic metal centers. CO_2 cycloaddition products of imidotitanium complexes are not stable, although the products of imido group transfer are clearly observed. Monoalkyl cations derived from $M(O_2{}^RNN')R_2$ appear to be dimeric for M = Ti and R = Me, and the propagating species in living polymerization catalysts derived from $M(O_2{}^RNN')R_2$, and their analogues in general, might also be dimeric, at least in the resting state. This stabilizing effect might clearly have implications with regard to the long lifetime and living nature of such catalyst systems.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Protio- and deutero-solvents were predried over activated 4 Å molecular sieves and were refluxed over the appropriate drying agent, distilled, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^1H, $^{13}C\{^1H\}$, ^{13}C, and ^{19}F NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers. ^1H and ^{13}C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two-dimensional $^1H-^1H$ and $^{13}C-^1H$ NMR experiments. ^1H and ^{13}C 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 referenced externally to $CFCl_3$ ^{19}F. Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as KBr pellets or as Nujol mulls between NaCl plates and were recorded on Perkin-Elmer 1600 and 1710 series FTIR spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of the University of Oxford Inorganic Chemistry Laboratory or Dyson Perrins Laboratory, and elemental analyses by the analytical services of the University of Oxford Inorganic Chemistry Laboratory. GPC polymer analysis was performed by Rapra Technology Ltd.

Literature Preparations and Other Starting Materials. The compounds $H_2O_2{}^{tBu}NN'$,[20] $H_2O_2{}^{Me}NN'$,[7] $Na_2O_2{}^{tBu}NN'$,[7] $Na_2O_2{}^{Me}NN'$,[7] $H_2O_2{}^{tBu}N$,[10] $[Ti(NR)Cl_2(py)_3]$ (R = ^tBu, 2,6-$C_6H_3Me_2$, 2,6-$C_6H_3{}^iPr_2$),[36] $Sc(CH_2SiMe_3)_3(THF)_2$,[40] $Y(CH_2SiMe_3)_3(THF)_2$,[40] and $TiCl_4(THF)_2$[41] were prepared according to published methods. The compounds $BAr^F{}_3$, $[Ph_3C][BAr^F{}_4]$, and $[HNMe_2Ph][BAr^F{}_4]$ were provided by DSM Research, and MAO was provided by Albermarle. 1-Hexene, pyridine, $^tBuNH_2$, and anilines were dried over the appropriate drying agents and distilled under reduced pressure. All other compounds and reagents were purchased and used without further purification.

$Na_2O_2{}^{tBu}N$ (1). To a stirred suspension of NaH (0.48 g, 20.2 mmol) in THF (20 mL) was added a stirred solution of $H_2O_2{}^{tBu}N$ (2.50 g. 5.04 mmol) in THF (20 mL) dropwise at −80 °C. Upon warming to room temperature, a gas (presumably H_2) was evolved. The cloudy gray solution was stirred at room temperature for 24 h. The resulting solution was filtered, volatiles were removed under reduced pressure, and the resulting cream powder was dried under reduced pressure. Yield: 2.49 g (92%). An analytically pure sample of **1**·THF was obtained by recrystallization from a saturated THF/pentane solution at −30 °C.

^1H NMR (pyridine-d_5, 300.0 MHz, 293 K): 7.51 (2H, d, ^4J = 2.5 Hz, 4-$C_6H_2{}^tBu_2$), 7.27 (2H, d, ^4J = 2.5 Hz, 6-$C_6H_2{}^tBu_2$), 4.6−3.8 (4H, br s, $CH_2C_6H_2{}^tBu_2$), 2.67 (2H, m, $CH_2CH_2CH_3$), 1.67 (20H, overlapping s and m, 3-$C_6H_2{}^tBu_2$ and $CH_2CH_2CH_3$), 1.46 (18H, s, 5-$C_6H_2{}^tBu_2$), 0.66 (3H, t, ^3J = 7.0 Hz, $CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 75.5 MHz, 293 K): 168.3 (2-$C_6H_2{}^tBu_2$), 137.4 (1-$C_6H_2{}^tBu_2$), 130.5 (3-$C_6H_2{}^tBu_2$), 127.8 (5-$C_6H_2{}^tBu_2$), 127.1 (6-$C_6H_2{}^tBu_2$), 123.1 (4-$C_6H_2{}^tBu_2$), 60.8 ($CH_2C_6H_2{}^tBu_2$), 53.0 ($CH_2CH_2CH_3$), 36.2 ($C_6H_2(CMe_3)_2$), 34.4 ($C_6H_2(CMe_3)_2$), 33.0 ($C_6H_2(CMe_3)_2$), 30.5 ($C_6H_2(CMe_3)_2$), 16.3 ($CH_2CH_2CH_3$), 12.7 ($CH_2CH_2CH_3$). IR data (KBr pellet, cm^{-1}): 2956 (s), 2870 (s), 1602 (w), 1434 (s), 1414 (s), 1382 (w), 1360 (s), 1314 (s), 1258 (m), 1234 (m), 1200 (m), 1160 (w), 1050 (m), 1024 (w), 882 (m), 828 (w), 804(w), 734 (w), 642 (w), 512 (w). Anal. Found (calcd for $C_{33}H_{51}NNa_2O_2 \cdot C_4H_8O$): C 72.3 (72.6), H 9.6 (9.7), N 2.5 (2.3).

$Sc(O_2{}^{tBu}NN')Cl(py)$ (2). To a stirred slurry of $ScCl_3$ (0.820 g, 1.39 mmol) in THF (30 mL), cooled to −78 °C, was added dropwise a solution of $Na_2O_2{}^{tBu}NN'$ (0.211 g, 1.39 mmol) in THF (30 mL). Shortly afterward an excess of pyridine (10 mL) was added. The solution was stirred at −78 °C for 1 h and was then allowed to warm to room temperature. After 16 h the volatiles were removed under reduced pressure. The product was extracted into benzene (40 mL), filtered, and concentrated to 5 mL to give a white powder, from which the mother liquor was decanted. Subsequent washing with pentane (2 × 25 mL) and drying in vacuo gave **2** as a white powder. Yield: 0.577 g (59%). Diffraction-quality crystals were grown by slow evaporation of a benzene solution.

^1H NMR (toluene-d_8, 500.0 MHz, 279 K): 9.29 (1H, d, ^3J 5.0 Hz, 6-C_5H_4N), 9.26 (2H, d, ^3J 5.0 Hz, 2-C_5H_5N), 7.42 (2H, d, ^4J 2.0 Hz, 4-$C_6H_2{}^tBu_2$), 6.97 (2H, d, ^4J 2.0 Hz, 6-$C_6H_2{}^tBu_2$), 6.75 (1H, t, ^3J 7.5 Hz, 4-C_5H_5N), 6.48−6.33 (3H, overlapping 2 × m, 3-C_5H_5N and 4-C_5H_4N), 6.14 (1H, app. t, app. ^3J 6.5 Hz, 5-C_5H_4N), 5.68 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.92 (2H, d, ^2J 12.5 Hz, NCH_2Ar distal to C_5H_4N), 3.29 (2H, s, $NCH_2C_5H_4N$), 2.79 (2H, d, ^2J 12.5 Hz, NCH_2Ar proximal to C_5H_4N), 1.80 (18H, s, 3-$C_6H_2{}^tBu_2$), 1.41 (18H, s, 5-$C_6H_2{}^tBu_2$). $^{13}C\{^1H\}$ NMR (toluene-d_8, 125.7 MHz, 279 K): 161.2 (2-$C_6H_2{}^tBu_2$)), 157.9 (2-C_5H_4N), 150.9 (6-C_5H_4N), 150.6 (2-C_5H_5N), 139.0 (3-C_5H_5N), 138.0 (4-C_5H_4N), 136.5 (3-$C_6H_2{}^tBu_2$), 125.4 (4-C_5H_5N), 124.7 (6-$C_6H_2{}^tBu_2$), 124.1 (4-$C_6H_2{}^tBu_2$), 123.4 (1-$C_6H_2{}^tBu_2$), 121.4 (5-C_5H_4N), 120.6 (3-C_5H_4N), 64.2 (NCH_2Ar), 57.1 ($NCH_2C_5H_4N$), 35.4 (3-$C_6H_2(CMe_3)_2$), 34.2 (5-$C_6H_2(CMe_3)_2$), 32.2 (5-$C_6H_2(CMe_3)_2$), 30.3 (3-$C_6H_2(CMe_3)_2$), 5-$C_6H_2{}^tBu_2$ not observed, possibly obscured or overlapping with solvent or other compound resonances. IR (NaCl plates, Nujol mull, cm^{-1}): 1869 (w), 1845 (w), 1829 (w), 1811(vw), 1793 (vw), 1772 (w), 1761 (vw), 1749 (w), 1734 (w), 1717 (w), 1698 (w), 1684 (w), 1670 (w), 1663 (vw), 1654 (w), 1647 (w), 1636 (vw), 1605 (vs), 1569 (w), 1559 (w), 1541 (m), 1522 (w), 1508 (m), 1446 (vs), 1417 (s), 1362 (s), 1340 (w), 1322 (m), 1307 (s), 1281 (s), 1240 (m), 1215 (m), 1204 (m), 1170 (m), 1155 (w), 1132 (m), 1099 (w), 1070 (w), 1054 (m), 1039 (w), 1019 (w), 1012 (m), 974 (m), 949 (vw), 932 (m),

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915 (m), 880 (m), 839 (s), 777 (w), 753 (s), 702 (m), 683 (vs), 633 (s). EIMS: *m/z* 623 (100%), [M − C_5H_5N]$^+$. Anal. Found (calcd for $C_{41}H_{55}ClN_2O_2Sc{\cdot}1.2(C_6H_6)$): C, 72.9 (72.7); H, 7.9 (7.7); N, 5.0 (5.3).

$Sc_2(O_2{}^{Me}NN')_2Cl_2$ (3). To a stirred slurry of $ScCl_3$ (0.205 g, 1.36 mmol) in THF (25 mL), cooled to −78 °C, was added dropwise a solution of $Na_2O_2{}^{Me}NN'{\cdot}0.3THF$ (0.600 g, 1.36 mmol) in THF (20 mL). The mixture was allowed to warm to room temperature and was stirred for 16 h. The volatiles were removed under reduced pressure and the residues extracted into dichloromethane (50 mL), filtered, and concentrated to 25 mL, after which hexanes (20 mL) were added. Cooling to −80 °C for 16 h produced a white precipitate, from which the mother liquor was decanted. The white powder was dried in vacuo to give **3**. Yield: 0.285 g (45%). Diffraction-quality crystals were grown by slow evaporation of a dichloromethane solution.

^{1}H NMR (benzene-d_6, 300.1 MHz, 293 K): 9.14 (2H, d, ^3J 4.5 Hz, 6-C_5H_4N), 7.40 (2H, app. td, app. ^3J 7.5 Hz, ^4J 1.5 Hz, 4-C_5H_4N), 6.88 (2H, app. t, app. ^3J 6.5 Hz 5-C_5H_4N), 6.79 (2H, s, 4-$C_6\mathit{H}_2Me_2$ (a)), 6.76 (2H, s, 6-$C_6\mathit{H}_2Me_2$ (a)), 6.70 (2H, d, ^3J 7.0 Hz, 3-C_5H_4N), 6.61 (2H, s, 6-$C_6\mathit{H}_2Me_2$ (b)), 6.40−6.35 (3H, overlapping m, 4-$C_6\mathit{H}_2Me_2$ (b) and NCH_2), 5.00 (2H, d, ^2J 14.0 Hz, NCH_2), 4.34 (2H, d, ^2J 15.5 Hz, NCH_2), 3.37 (2H, d, ^2J 14.0 Hz, NCH_2), 3.25−3.17 (4H, overlapping m, 2 × NCH_2), 2.20 (6H, s, 3-$C_6H_2\mathit{Me}_2$ (a)), 2.01 (6H, s, 3-$C_6H_2\mathit{Me}_2$ (b)), 1.86 (6H, s, 5-$C_6H_2\mathit{Me}_2$ (b)), 1.81 (6H, s, 5-$C_6H_2\mathit{Me}_2$ (a)). $^{13}C\{^1H\}$ NMR (benzene-d_6, 125.7 MHz, 293 K): 159.7 (2-C_5H_4N), 159.0 (2-$\mathit{C}_6H_2Me_2$ (a)) 155.7 (2-$\mathit{C}_6H_2Me_2$ (b)), 150.6 (6-C_5H_4N), 139.1 (4-C_5H_4N), 132.4 (4-$\mathit{C}_6H_2Me_2$ (b)), 131.5 (4-$\mathit{C}_6H_2Me_2$ (a)), 129.8 (5-$\mathit{C}_6H_2Me_2$ (b)), 129.5 (6-$\mathit{C}_6H_2Me_2$ (b)), 128.2 (6-$\mathit{C}_6H_2Me_2$ (a)), 127.8 (3-$\mathit{C}_6H_2Me_2$ (b)), 126.1 (5-$\mathit{C}_6H_2Me_2$ (a)), 125.9 (3-$\mathit{C}_6H_2Me_2$ (a)), 125.5 (1-$\mathit{C}_6H_2Me_2$ (b)), 122.6 (1-$\mathit{C}_6H_2Me_2$ (a)), 122.4 (5-C_5H_4N), 121.9 (3-C_5H_4N), 65.5 (NCH_2), 63.5 (NCH_2), 60.3 (NCH_2), 20.5 (5-$C_6H_2\mathit{Me}_2$ (a)), 20.1 (5-$C_6H_2\mathit{Me}_2$ (b)), 16.4 (3-$C_6H_2\mathit{Me}_2$ (b)), 16.0 (3-$C_6H_2\mathit{Me}_2$ (a)), the designations (a) and (b) relate groups of resonances for the same phenoxy groups. IR (KBr plates, Nujol mull, cm^{-1}): 1608 (m), 1572 (w), 1484 (vs), 1397 (w), 1350 (w), 1311 (s), 1278 (s), 1261 (m), 1215 (s), 1205 (m), 1153 (s), 1099 (m), 1057 (w), 1017 (m), 974 (m), 963 (w), 945 (w), 902 (w), 852 (s), 838 (m), 791 (s), 756 (m), 643 (w), 625 (m), 579 (m), 554 (m). EI-HRMS: *m/z* found (calcd for $C_{48}H_{52}Cl_2N_4O_4Sc_2$, [M]$^+$) 908.2496 (908.2484). Anal. Found (calcd for $C_{48}H_{52}Cl_2N_4O_4Sc_2$): C, 63.5 (63.4); H, 6.1 (5.8); N, 6.3 (6.2).

$Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2$ (4). To a stirred solution of YCl_3 (0.232 g, 1.19 mmol) in pyridine (35 mL), cooled to −30 °C, was added dropwise a solution of $Na_2O_2{}^{tBu}NN'$ (0.700 g, 1.19 mmol) in pyridine (25 mL). The solution was allowed to warm to room temperature and was stirred for 16 h, after which the volatiles were removed under reduced pressure to give a cream powder. This was extracted into benzene (40 mL) and filtered, and the solution was concentrated to 20 mL, after which pentane (20 mL) was added. Cooling the solution to −30 °C for 16 h produced a bright white precipitate, from which the mother liquor was filtered. The powder was washed with pentane (2 × 25 mL) and dried under reduced pressure to give **4**. Yield: 0.657 g (74%). Diffraction-quality crystals were grown from a saturated benzene solution at room temperature.

^{1}H NMR (dichloromethane-d_2, 300.1 MHz, 293 K): 9.06 (4H, dd, ^3J 6.0 Hz, ^4J 1.5, Hz 2-C_5H_5N), 8.84 (2H, d, ^3J 4.5 Hz, 6-C_5H_4N), 7.93 (2H, t, ^3J 7.5 Hz, 4-C_5H_5N), 7.50 (4H, app. td, app.^3J 6.0 Hz, ^4J 1.0 Hz, 3-C_5H_5N), 7.36 (2H, app. td, app. ^3J 8.0 Hz, ^4J 1.5 Hz, 4-C_5H_4N), 7.05 (4H, d, ^4J 2.5, 4-$C_6\mathit{H}_2{}^tBu_2$), 6.97 (2H, app. t, app. ^3J 5.5 Hz, 5-C_5H_5N), 6.90 (4H, d, ^4J 2.5, 6-$C_6\mathit{H}_2{}^tBu_2$), 6.64 (2H, d, ^3J 8.0 Hz, 3-C_5H_4N), 4.16 (4H, d, ^2J 11.5 Hz, NCH_2Ar), 3.76 (4H, s, $NC\mathit{H}_2C_5H_4N$), 3.30 (4H, d, ^2J 12.5 Hz, NCH_2Ar), 1.39 (36H, s, 3-$C_6H_2{}^t\mathit{Bu}_2$), 1.24 (36H, s, 5-$C_6H_2{}^t\mathit{Bu}_2$). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 125.7 MHz, 293 K): 160.5 (2-$\mathit{C}_6H_2{}^tBu_2$), 158.9 (2-C_5H_4N), 149.8 (2-C_5H_5N), 149.7 (6-C_5H_4N), 139.0 (4-C_5H_5N), 138.3 (4-C_5H_4N), 136.6 (5-$\mathit{C}_6H_2{}^tBu_2$), 135.4 (3-$\mathit{C}_6H_2{}^tBu_2$), 125.2 (4-$\mathit{C}_6H_2{}^tBu_2$), 124.8 (3-C_5H_5N), 123.8 (6-$\mathit{C}_6H_2{}^tBu_2$), 123.0 (1-$\mathit{C}_6H_2{}^tBu_2$), 122.0 (5-C_5H_4N), 121.7 (3-C_5H_4N), 64.1 ($N\mathit{C}H_2C_5H_4N$), 53−51 (very broad $N\mathit{C}H_2Ar$), 35.3 (3-$C_6H_2(\mathit{C}Me_3)_2$), 34.2 (5-$C_6H_2(\mathit{C}Me_3)_2$), 32.1 (5-$C_6H_2(C\mathit{Me}_3)_2$), 30.2 (3-$C_6H_2(C\mathit{Me}_3)_2$). IR (KBr plates, Nujol mull, cm^{-1}): 2280 (vw), 1861 (vw), 1765 (vw), 1726 (vw), 1711 (vw), 1693 (vw), 1659 (vw), 1603 (vs), 1571 (m), 1513 (w), 1446 (s), 1415 (s), 1361 (s), 1329 (s), 1303 (vs), 1289 (s), 1277 (s), 1240 (s), 1221 (w), 1204 (m), 1169 (m), 1153 (m), 1135 (m), 1096 (m), 1070 (s), 1056 (m), 1038 (s), 1026 (m), 1011 (s), 980 (w), 984 (w), 943 (w), 915 (w), 877 (s), 863 (m), 837 (s), 781 (w), 762 (m), 751 (s), 700 (s), 646 (m), 626 (m). Found (calcd for $C_{82}H_{110}Cl_2N_6O_4Y_2$): C, 66.4 (66.0); H, 7.5 (7.6); N, 5.8 (5.6).

$Sc(O_2{}^{tBu}NN')(CH_2SiMe_3)(THF)$ (5). To a solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.250 g, 0.597 mmol) in THF (25 mL), cooled to −78 °C, was added dropwise a solution of $H_2O_2{}^{tBu}NN'$ (0.325 g. 0.597 mmol) in THF (15 mL). The solution was then allowed to warm to room temperature and was stirred for a further 2 h, after which the volatiles were removed under reduced pressure to give a pale yellow powder. This was extracted into pentane (3 × 20 mL) and filtered, and the solution was concentrated to 30 mL. Cooling to −80 °C for 16 h gave a white powder, from which the mother liquor was decanted. The white powder was dried in vacuo to give **5**. Yield: 0.255 g (63%).

^{1}H NMR (benzene-d_6, 300.1 MHz, 293 K): 8.72 (1H, d, ^3J 4.5 Hz, 6-C_5H_4N), 7.36 (2H, d, ^4J 2.5 Hz, 4-$C_6\mathit{H}_2{}^tBu_2$, 6.95 (2H, d, ^4J 2.5 Hz, 6-$C_6\mathit{H}_2{}^tBu_2$, 6.39 (1H, app.td, app. ^3J 8.0 Hz, ^4J 1.5 Hz, 4-C_5H_4N, 6.12 (1H, at, a ^3J 6.0 Hz, 5-C_5H_4N, 5.72 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N, 4.04 (4H, br s, 2-C_4H_8O, 3.09 (2H, d, ^2J 12.5 Hz, $NC\mathit{H}_2Ar$ distal to C_5H_4N, 3.13 (2H, s, $NC\mathit{H}_2C_5H_4N$, 2.85 (2H, d, ^2J 12.5 Hz, $NC\mathit{H}_2Ar$ proximal to C_5H_4N, 1.68 (18H, s, 3-$C_6H_2{}^t\mathit{Bu}_2$, 1.36 (18H, s, 5-$C_6H_2{}^t\mathit{Bu}_2$, 1.22 (4H, br m, 3-C_4H_8O, 0.55 (9H, s, $CH_2Si\mathit{Me}_3$, 0.40 (2H, s, $C\mathit{H}_2SiMe_3$. $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 161.6 (2-$\mathit{C}_6H_2{}^tBu$), 159.0 (2-C_5H_4N), 149.6 (6-C_5H_4N), 137.5 (4-C_5H_4N), 136.8 (5-$\mathit{C}_6H_2{}^tBu_2$), 136.3 (3-$\mathit{C}_6H_2{}^tBu_2$), 124.9 (4-$\mathit{C}_6H_2{}^tBu_2$), 124.1 (6-$\mathit{C}_6H_2{}^tBu_2$), 123.6 (1-$\mathit{C}_6H_2{}^tBu_2$), 121.2 (5-C_5H_4N), 121.1 (3-C_5H_4N), 69.6 (2-C_4H_8O), 64.4 ($N\mathit{C}H_2Ar$), 57.1 ($N\mathit{C}H_2C_5H_4N$), 35.5 (3-$C_6H_2(\mathit{C}Me_3)_2$), 34.1 (5-$C_6H_2(\mathit{C}Me_3)_2$), 32.2 (5-$C_6H_2(C\mathit{Me}_3)_2$), 30.4 (3-$C_6H_2(C\mathit{Me}_3)_2$), 4.0 ($\mathit{C}H_2SiMe_3$), 0.0 ($CH_2Si\mathit{Me}_3$), 3-C_4H_8O not observed, possibly obscured or overlapping other compound resonances. IR (KBr plates, Nujol mull, cm^{-1}): 2350 (w), 2284 (w), 1606 (s), 1570 (m), 1416 (s), 1321 (m), 1307 (s), 1237 (s), 1203 (m), 1168 (m), 1156 (w), 1132 (m), 1103 (m), 1069 (m), 1057 (m), 1019 (s), 974 (m), 934 (w), 915 (m), 868 (vs), 844 (s), 779 (w), 746 (s), 723 (s), 668 (m), 645 (m), 631 (w), 546 (m). EIMS: *m/z* 587 (65%), [M − CH_2SiMe_3, − THF]$^+$. Anal. Found (calcd for $C_{44}H_{69}N_2O_3ScSi$): C, 71.0 (70.7); H, 9.0 (9.3); N, 4.2 (3.8).

$Y(O_2{}^{tBu}NN')(CH_2SiMe_3)(THF)$ (6). To a stirred solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.500 g, 1.01 mmol) in benzene (20 mL), cooled to 7 °C, was added dropwise a solution of $H_2O_2{}^{tBu}NN'$ (0.550 g, 1.01 mmol) in benzene (15 mL). The solution was allowed to warm to room temperature and then stirred for 16 h. The volatiles were removed under reduced pressure to give **6** as a cream powder, which was dried in vacuo. Yield: 0.613 g (77%). Attempts to recrystallize this compound led to sample degradation.

^{1}H NMR (dichloromethane-d_2, 500.0 MHz, 293 K): 8.57 (1H, d, ^3J 5.0 Hz, 6-C_5H_5N), 7.29 (1H, app. td, app. ^3J 8.0 Hz, ^4J 2.0 Hz, 4-C_5H_4N), 7.02 (2H, d, ^4J 2.5 Hz, 4-$C_6\mathit{H}_2{}^tBu_2$), 6.93−6.88 (3H, overlapping m, 6-$C_6\mathit{H}_2{}^tBu$ and 5-C_5H_4N), 6.57 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 4.36 (4H, br s, 2-C_4H_8O), 4.10 (2H, d, ^2J 12.0 Hz, $NC\mathit{H}_2Ar$ distal to C_5H_4N), 3.63 (2H, s, $NC\mathit{H}_2C_5H_4N$), 3.23 (2H, d, ^2J 12.0 Hz, $NC\mathit{H}_2Ar$ proximal to C_5H_4N), 2.02 (2H, br m, 3-C_4H_8O), 1.37 (18H, s, 3-$C_6H_2{}^t\mathit{Bu}_2$), 1.23 (18H, s, 5-$C_6H_2{}^t\mathit{Bu}_2$), 0.06 (9H, s, $CH_2Si\mathit{Me}_3$), −0.56 (2H, d, $^2J_{Y-H}$ 3.0 Hz, $C\mathit{H}_2SiMe_3$). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 75.5 MHz, 293 K): 166.3 (2-$\mathit{C}_6H_2{}^tBu_2$), 164.8 (2-C_5H_4N), 154.1 (6-C_5H_4N), 142.8 (4-C_5H_4N), 140.9 (5-$\mathit{C}_6H_2{}^tBu_2$), 140.4 (3-$\mathit{C}_6H_2{}^tBu_2$), 133.1

(6-$C_6H_2{}^tBu_2$),), 130.3 (4-$C_6H_2{}^tBu_2$), 128.2 (1-$C_6H_2{}^tBu_2$), 126.9 (3-C_5H_4N), 126.3 (5-C_5H_4N), 71.9 (2-C_4H_8O), 64.2 (NCH_2Ar), 57.3 ($NCH_2C_5H_4N$), 39.7 (3-$C_6H_2(CMe_3)_2$), 38.5 (5-$C_6H_2(CMe_3)_2$), 36.5 (5-$C_6H_2(CMe_3)_2$), 34.5 (3-$C_6H_2(CMe_3)_2$), 30.2 (3-C_4H_8O), 8.8 (CH_2SiMe_3), 5.6 (CH_2SiMe_3). IR (KBr plates, Nujol mull, cm^{-1}): 2361 (w), 2342 (w), 2005 (vw), 1952 (vw), 1773 (vw), 1732 (vw), 1605 (s), 1568 (m), 1415 (s), 1361 (s), 1318 (vs), 1306 (s), 1236 (s), 1202 (m), 1167 (m), 1155 (w), 1131 (m), 1101 (s), 1105 (s), 1018 (vs), 967 (m), 948 (vw), 932 (w), 912 (m), 902 (m), 872 (s), 835 (vs), 806 (vs), 780 (m), 762 (s), 743 (s), 721 (m), 676 (s), 644 (m), 629 (w), 601 (m). Anal. Found (calcd for $C_{44}H_{69}N_2O_3SiY$): C, 65.3 (67.0); H, 8.5 (8.6); N 3.5 (3.6).

$Sc(O_2{}^{tBu}NN')\{PhC(NSiMe_3)_2\}$ (7). To a slurry of $ScCl_3$ (0.1285 g, 0.8492 mmol) in THF (25 mL), cooled to −78 °C, was added dropwise a solution of $Na_2O_2{}^{tBu}NN$ (**3**) (0.500 g, 0.849 mmol) in THF (20 mL). The solution was stirred at −78 °C for 20 min, after which time it was allowed to warm to room temperature and was stirred for a further 90 min. The solution was then again cooled to −78 °C for the dropwise addition of a solution of $Li[PhC(NSiMe_3)_2]$ (0.229 g, 0.849 mmol) in THF (15 mL). The solution was stirred at −78 °C for 20 min, after which time it was allowed to warm to room temperature and was then stirred for a further 3 h. The volatiles were removed under reduced pressure to yield a white powder. This was extracted into pentane (50 mL) and filtered, and the solution was concentrated to 10 mL. Cooling to −30 °C for 16 h produced a white precipitate, from which the mother liquor was decanted. The white powder was dried in vacuo to give **7**. Yield: 0.313 g (43%).

^1H NMR (dichloromethane-d_2, 300.1 MHz, 213 K): 8.30 (1H, d, ^3J 5.0 Hz, 6-C_5H_4N), 7.44 (1H, app. td, app. ^3J 7.5 Hz, ^4J 1.0 Hz, 4-C_5H_4N), 7.32 (3H, m, *o*- or *m*-, and *p*-C_6H_5), 7.18 (2H, m, *o*- or *m*-C_6H_5), 7.05 (1H, app. t, app. ^3J 6.0 Hz, 5-C_5H_4N), 6.94 (2H, br s, 4-$C_6H_2{}^tBu_2$), 6.89 (2H, s, 6-$C_6H_2{}^tBu_2$), 6.71 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 4.00 (2H, s, $NCH_2C_5H_4N$), 3.85 (2H, br d, ^2J 11.0 Hz, NCH_2Ar distal to C_5H_4N), 3.66 (2H, vbr s, NCH_2Ar proximal to C_5H_4N), 1.32 (18H, br s, 3-$C_6H_2{}^tBu_2$), 1.19 (18H, s, 5-$C_6H_2{}^tBu_2$), −0.08 (9H, s, $NSiMe_3$ (a)), −0.58 (9H, s, $NSiMe_3$ (b)), which $NSiMe_3$, designated (a) and (b), lies *cis* and which lies *trans* to the pyridyl donor could not be determined. $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 125.7 MHz, 213 K): 181.4 ($C_6H_5C(NSiMe_3)_2$), 160.4 (2-$C_6H_2{}^tBu_2$), 156.6 (2-C_5H_4N), 146.6 (6-C_5H_4N), 142.1 (*i*-C_6H_5), 138.3 (4-C_5H_4N), 136.2 (5- or 3-$C_6H_2{}^tBu_2$), 134.2 (5- or 3-$C_6H_2{}^tBu_2$), 127.5 (*o*- or *m*-, and *p*-C_6H_5), 126.3 (*o*- or *m*- C_6H_5), 124.5 (6-$C_6H_2{}^tBu_2$), 123.0 (1-$C_6H_2{}^tBu_2$), 122.9 (4-$C_6H_2{}^tBu_2$), 121.7 (5-C_5H_4N), 120.7 (3-C_5H_4N), 61.4 ($NCH_2C_5H_4N$), 33.5 (3-$C_6H_2(CMe_3)_2$), 33.5 (5-$C_6H_2(CMe_3)_2$), 31.2 (5-$C_6H_2(CMe_3)_2$), 29.4 (3-$C_6H_2(CMe_3)_2$), 2.0 ($NSiMe_3$ (a)), 1.7 ($NSiMe_3$ (b)), NCH_2py not observed, possibly overlapping other compound resonances. IR (KBr plates, Nujol mull, cm^{-1}): 2359 (w), 1893 (vw), 1869 (vw), 1845 (vw), 1772 (vw), 1734 (vw), 1717 (vw), 1698 (vw), 1653 (w), 1610 (m), 1572 (m), 1559 (vw), 1541 (vw), 1417 (m), 1361 (m), 1336 (w), 1322 (s), 1304 (s), 1245 (s), 1203 (m), 1170 (m), 1155 (w), 1131 (m), 1103 (m), 1056 (w), 1034 (m), 1018 (s), 1005 (s), 995 (m), 972 (w), 952 (w), 934 (w), 924 (m), 914 (w), 898 (w), 874 (m), 867 (m), 842 (vs), 793 (m), 765 (s), 754 (s), 709 (m), 686 (w), 645 (w), 546 (m). EI-HRMS: *m/z* found (calcd for $C_{49}H_{73}N_4O_2Si_2Sc$, $[M]^+$) 850.5013 (850.4831). Anal. Found (calcd for $C_{49}H_{73}N_4O_2Si_2Sc$): C, 68.9 (69.1); H, 8.5 (8.6); N, 6.5 (6.6).

$Sc(O_2{}^{Me}NN')\{PhC(NSiMe_3)_2\}$ (8). To a stirred slurry of $Sc_2(O_2{}^{tBu}NN')_2Cl_2$ (**3**) (0.185 g 1.97 mmol) in THF (25 mL), cooled to −78 °C, was added dropwise a solution of $Li[PhC(NSiMe_3)_2]$ (0.532 g 1.970 mmol) in THF (15 mL). The solution was allowed to warm to room temperature and stirred for 1 h, after which time the volatiles were removed under reduced pressure. The product was extracted into pentane (50 mL) and filtered, and the solution was concentrated to 20 mL. Cooling to −30 °C produced a white precipitate from which the mother liquor decanted. The product was washed with pentane at −78 °C (2 × 10 mL) and dried in vacuo to give **8**. Yield: 0.110 g (41%).

^1H NMR (dichloromethane-d_2 300.1 MHz, 293 K): 8.46 (1H, d, ^3J 4.5 Hz, 6-C_5H_4N), 7.52 (1H, app. td, app. ^3J 7.5 Hz, ^4J 1.5 Hz, 4-C_5H_4N), 7.39−7.33 (3H, overlapping m, *o*- or *m*-, and *p*-C_6H_5), 7.28−7.24 (2H, m, *o*- or *m*-C_6H_5), 7.12 (1H, app. t, app. ^3J 6.5 Hz, 5-C_5H_4N), 6.83 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 6.66 (4H, overlapping s, 4- and 6-$C_6H_2Me_2$), 4.01 (2H, s, $NCH_2C_5H_4N$), 3.69 (2H, d, ^2J 12 Hz, NCH_2Ar distal to C_5H_4N), 3.58 (2H, d, ^2J 12 Hz, NCH_2Ar proximal to C_5H_4N), 2.13 (6H, s, 3-$C_6H_2Me_2$), 2.03 (6H, s, 5-$C_6H_2Me_2$), −0.24 18H, s, $SiNMe_3$). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 75.5 MHz, 293 K): 182.1 ($C_6H_5C(NSiMe_3)_2$), 160.3 (2-$C_6H_2Me_2$), 157.4 (2-C_5H_4N), 145.8 (6-C_5H_4N), 142.7 (*i*-C_6H_5), 138.7 (4-C_5H_4N), 131.4 (5- or 3-$C_6H_2Me_2$), 128.1 (5- or 3-$C_6H_2Me_2$), 128.0 (*o*- or *m*-, or *p*-C_6H_5), 127.9 (*o*- or *m*-, or *p*-C_6H_5), 126.8 (*o*- or *m*-C_6H_5), 125.3 (6-$C_6H_2Me_2$), 124.1 (1-$C_6H_2Me_2$), 123.1 (4-$C_6H_2Me_2$), 122.7 (5-C_5H_4N), 121.7 (3-C_5H_4N), 62.9 ($NCH_2C_5H_4N$), 62.0 (NCH_2Ar), 20.4 (3-$C_6H_2Me_2$), 16.9 (5-$C_6H_2Me_2$), 2.1 ($NSiMe_3$). IR (KBr plates, Nujol mull, cm^{-1}): 2727 (vw), 2361 (m), 1869 (vw), 1845 (vw), 1829 (vw), 1793 (vw), 1772 (w), 1749 (w), 1734 (vw), 1717 (vw), 1699 (vw), 1684 (vw), 1670 (vw), 1654 (w), 1636 (vw), 1608 (m), 1570 (vw), 1559 (vw), 1542 (w), 1522 (vw), 1508 (m), 1341 (w), 1323 (m), 1312 (m), 1291 (w), 1260 (m), 1245 (m), 1162 (bm), 1021 (m), 1006 (m), 995 (m), 964 (w), 946 (vw), 838 (vs), 757 (s), 700 (w), 593 (vw). EIMS: *m/z* 665 (37%), $[M, -CH_3, -2H]^+$; *m/z* 574 (9%), $[M, -C_6H_5, -2CH_3]^+$. Anal. Found (calcd for $C_{37}H_4$

$Ti(O_2{}^{tBu}NN')Cl_2$ (9). To a stirred yellow solution of $TiCl_4(THF)_2$ (1.312 g, 3.93 mmol) in diethyl ether (40 mL) cooled to −40 °C was added dropwise a solution of MeLi (1.6 M in Et_2O, 4.91 mL, 7.93 mmol). The solution was stirred for 1 h at −40 °C. To this solution was added dropwise a solution of $H_2O_2{}^{tBu}NN'$ (2.140 g, 3.93 mmol) in diethyl ether (40 mL). The solution was allowed to stir for 1 h at −40 °C before warming to room temperature. After stirring for a further 1 h the volatiles were removed under reduced pressure. The residues were extracted with dichloromethane (100 mL), filtered, and concentrated to 30 mL, and hexanes (30 mL) were added. Cooling to −80 °C produced a dark orange precipitate, from which the mother liquor was decanted. This was washed with cold hexanes (2 × 30 mL) and dried in vacuo to give **9**. Yield: 3.67 g (70%). Diffraction-quality crystals were grown by slow evaporation of a dichloromethane solution.

^1H NMR (benzene-d_6, 300.1 MHz, 293 K): 9.04 (1H, d, ^3J 6.0 Hz, 6-C_5H_4N), 7.55 (1H, d, ^4J 2.5 Hz, 4-$C_6H_2{}^tBu_2$ (a)), 7.06 (1H, d, ^4J 3.0 Hz, 6-$C_6H_2{}^tBu_2$ (a)), 7.01 (1H, d, ^4J 2.5 Hz, 4-$C_6H_2{}^tBu_2$ (b)), 6.46 (1H, app. td, a ^3J 7.5 Hz, app. ^4J 1.0 Hz, 4-C_5H_4N), 6.32 (1H, d, ^4J 3.0 Hz, 6-$C_6H_2{}^tBu_2$ (b)), 6.09 (1H, at, a ^3J 6.5 Hz, 5-C_5H_4N), 5.99 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 5.35 (1H, d, ^2J 13.0 Hz NCH_2Ar (a)), 4.51 (1H, d, ^2J 15.0 Hz, $NCH_2C_5H_4N$), 3.60 (1H, d, ^2J 13.0 Hz, NCH_2Ar (b)), 2.92 (1H, d, ^2J 13.5 Hz NCH_2Ar (a)), 2.90 (1H, d, ^2J 15.0 Hz, $NCH_2C_5H_4N$), 2.21 (1H, d, ^2J 13.0 Hz, NCH_2Ar (b)), 1.81 (9H, s, 3-$C_6H_2{}^tBu_2$ (a)), 1.58 (9H, s, 3-$C_6H_2{}^tBu_2$ (b)), 1.44 (9H, s, 5-$C_6H_2{}^tBu_2$ (a)), 1.16 (9H, s, 5-$C_6H_2{}^tBu_2$ (b)). Further resonances at 1.35 and 1.62 as well as other low-intensity and mostly obscured peaks indicate the presence of an isomer in which the aryl oxide rings are positioned *cis* to each other (i.e., C_s symmetry). These peaks relate to (18H, s, 5-$C_6H_2{}^tBu_2$) and (18H, s, 3-$C_6H_2{}^tBu_2$), respectively. The designations (a) and (b) relate resonances to protons on a specific phenoxy group; however which group lies *cis* and which *trans* to the pyridyl group could not be determined. $^{13}C\{^1H\}$ NMR (benzene-d_6, 125.7 MHz, 293 K): 160.5 (2-$C_6H_2{}^tBu_2$ (b)), 158.6 (2-$C_6H_2{}^tBu_2$ (a)), 155.8 (2-C_5H_4N), 149.6 (6-C_5H_4N), 144.4 (5-$C_6H_2{}^tBu_2$ (a)), 141.8 (5-$C_6H_2{}^tBu_2$ (b)), 138.1 (4-C_5H_4N), 137.1 (3-$C_6H_2{}^tBu_2$ (a)), 135.1 (3-$C_6H_2{}^tBu_2$ (b)), 126.9 (1-$C_6H_2{}^tBu_2$ (a)), 125.5 (1-$C_6H_2{}^tBu_2$ (b)), 124.1 (4-$C_6H_2{}^tBu_2$ (a)), 124.0 (6-$C_6H_2{}^tBu_2$ (a)), 123.5 (6-$C_6H_2{}^tBu_2$ (b)), 123.3 (4-$C_6H_2{}^tBu_2$ (b)), 122.5 (5-C_5H_4N), 122.5

(3-C_5H_4N), 65.7 ($NCH_2C_5H_4N$), 65.4 (NCH_2Ar (a)), 61.0 (NCH_2-Ar (b), 36.1 (3-$C_6H_2(CMe_3)_2$ (a)), 35.3 (3-$C_6H_2(CMe_3)_2$ (b)), 35.1 (5-$C_6H_2(CMe_3)_2$ (a)), 34.5 (5-$C_6H_2(CMe_3)_2$ (b)), 32.2 (5-$C_6H_2(CMe_3)_2$ (a)), 32.1 (5-$C_6H_2(CMe_3)_2$ (b)), 30.8 (3-$C_6H_2(CMe_3)_2$ (b)), 30.7 (3-$C_6H_2(CMe_3)_2$ (a)). IR (NaCl plates, Nujol mull, cm^{-1}): 2672 (m), 2360 (m), 2342 (m), 1610 (m), 1576 (w), 1559 (w), 1541 (w), 1522 (w), 1507 (w), 1295 (s), 1261 (s), 1241 (m), 1205 (m), 1171 (m), 1127 (w), 1025 (s), 975 (bm), 918 (s), 871 (s), 848 (s), 764 (m), 755 (m), 651 (w), 604 (w). EIMS: *m/z* 661 (35%), $[M]^+$; *m/z* 625 (100%), $[M - Cl]^+$. Anal. Found (calcd for $C_{36}H_{50}Cl_2N_2O_2Ti \cdot 0.6(C_7H_8)$): C, 67.2 (67.4); H, 7.4 (7.7); N, 3.6 (3.9).

Alternative Synthesis of $Ti(O_2{}^{tBu}NN')Cl_2$ (9). To a stirred brown solution of $Ti(NMe_2)Cl_2$ (0.395 g, 0.725 mmol) in benzene (25 mL), cooled to 7 °C, was added dropwise a solution of $H_2O_2{}^{tBu}NN'$ (0.150 g, 0.725 mmol) in benzene (25 mL). The solution was allowed to warm to room temperature and was stirred for 1 h, after which time the volatiles were removed under reduced pressure, giving a dark orange powder. This was dissolved in toluene (50 mL), the volume was reduced to 10 mL, and hexanes (30 mL) were added. Cooling of the solution to −80 °C produced a dark orange precipitate, which was washed with cold hexanes (2 × 30 mL) and dried in vacuo to give **9**. Yield: 0.221 g (46%).

Alternative NMR Tube Scale Synthesis of $Ti(O_2{}^{tBu}NN')Cl_2$ (9). To a solution of $Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (**11**) (0.030 g, 0.0044 mmol) in benzene-d_6 (0.75 mL) in a 5 mm J. Young NMR tube was added Me_3SiCl (0.0096 g, 0.0088 mmol). After 3 days an ^1H NMR spectrum confirmed that the reaction had proceeded quantitatively to give **9** and 2 equiv of Me_3SiNMe_2.

$Ti(O_2{}^{Me}NN')Cl_2$ (10). To a stirred solution of $TiCl_4(THF)_2$ (1.774 g, 5.31 mmol) in diethyl ether (40 mL), cooled to −40 °C, was added dropwise a solution of MeLi (1.6 M in Et_2O, 6.64 mL, 10.6 mmol). The solution was stirred for 1 h at −40 °C. To this was added dropwise a solution of $H_2O_2{}^{Me}NN'$ (2.00 g, 5.31 mmol) in diethyl ether (40 mL). The solution was stirred for 1 h at −40 °C, allowed to warm to room temperature, and then stirred for a further 1 h, after which time the volatiles were removed under reduced pressure. The residues were extracted into dichloromethane (100 mL) and filtered, and hexanes (50 mL) were added to the orange solution. Cooling to −30 °C for 16 h produced a dark orange precipitate, from which the mother liquor was decanted. The product was dried in vacuo at 80 °C for 16 h to give $Ti(O_2NN')Cl_2 \cdot nC_6H_{14}$ (**10**·nC_6H_{14}) (typical value of $n = 0.2$). Yield: 1.786 g (66%). The hexanes content *n* was determined by careful integration of the ^1H NMR spectrum. Diffraction-quality crystals were grown by slow evaporation of a benzene solution.

^1H NMR (dichloromethane-d_2, 300.1 MHz, 293 K): 9.07 (1H, app. dt, ^3J 5.5 Hz, app. ^4J 1.0 Hz, 6-C_5H_4N), 7.58 (1H, app. td, app. ^3J 7.5 Hz, ^4J 1.5 Hz, 4-C_5H_4N), 7.16 (1H, app. t, app. ^3J 6.5 Hz, 5-C_5H_4N), 6.98 (1H, s, 4-$C_6H_2Me_2$ (a)), 6.94 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 6.90 (1H, s, 6-$C_6H_2Me_2$ (a)), 6.60 (1H, s, 6-$C_6H_2Me_2$ (b)), 6.52 (1H, s, 4-$C_6H_2Me_2$ (b)), 5.18 (1H, d, ^2J 13.0 Hz, NCH_2Ar (b)), 4.85 (1H, d, ^2J 15.5 Hz, $NCH_2C_5H_4N$), 3.89 (1H, d, ^2J 13.0 Hz, NCH_2Ar (a)), 3.83 (1H, d, ^2J 15.5 Hz, $NCH_2C_5H_4N$), 3.56 (1H, d, ^2J 13.0 Hz, NCH_2Ar (b)), 3.04 (1H, d, ^2J 13.0 Hz, NCH_2Ar (a)), 2.36 (3H, s, 3-$C_6H_2Me_2$ (b)), 2.29 (3H, s, 5-$C_6H_2Me_2$ (b)), 2.05 (3H, s, 5-$C_6H_2Me_2$ (a)), 2.00 (3H, s, 3-$C_6H_2Me_2$ (a)). The designations (a) and (b) relate resonances to protons on a specific phenoxy group. However which group lies *cis* and which trans to the pyridyl group could not be determined. $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 125.7 MHz, 293 K): 160.9 (2-$C_6H_2Me_2$ (a)), 157.6 (2-$C_6H_2Me_2$ (b)), 156.1 (2-C_5H_4N), 148.4 (6-C_5H_4N), 139.6 (4-C_5H_4N), 132.3 (5-$C_6H_2Me_2$ (b)), 131.7 (4-$C_6H_2Me_2$ (b)), 131.6 (4-$C_6H_2Me_2$ (a)), 130.4 (5-$C_6H_2Me_2$ (a)), 127.7 (6-$C_6H_2Me_2$ (b)), 126.7 (6-$C_6H_2Me_2$ (a)), 125.8 (1-$C_6H_2Me_2$ (b)), 124.4 (1-$C_6H_2Me_2$ (a)), 124.2 (3-$C_6H_2Me_2$ (b)), 123.8 (3-$C_6H_2Me_2$ (a)), 123.6 (3-C_5H_4N), 121.8 (5-C_5H_4N), 66.0 ($NCH_2C_5H_4N$), 65.1 (NCH_2Ar (b)), 61.2 (NCH_2Ar (a)), 20.8 (5-$C_6H_2Me_2$ (b)), 20.5 (5-$C_6H_2Me_2$ (a)), 16.2 (3-$C_6H_2Me_2$ (b)), 15.7 (3-$C_6H_2Me_2$ (a)). IR (NaCl plates, Nujol mull, cm^{-1}): 1610 (m), 1294 (w), 1237 (s), 1220 (s), 1160 (s), 1059 (w), 1026 (w), 959 (w), 948 (w), 871 (s), 839 (s), 762 (w), 750 (w). EI-HRMS: *m/z* found (calcd for $C_{24}H_{26}Cl_2N_2O_2Ti$, $[M]^+$) 492.0856 (492.0851).

$Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (11). To a stirred yellow solution of $Ti(NMe_2)_4$ (0.513 g, 2.29 mmol) in benzene (40 mL), cooled to 7 °C, was added dropwise a solution of $H_2O_2{}^{tBu}NN'$ (1.247 g, 2.29 mmol) in benzene (50 mL). The solution was allowed to warm to room temperature and was stirred for 1 h, after which time the volatiles were removed under reduced pressure to give **11** as a rusty-orange powder. Yield: 1.37 g, (88%). Diffraction-quality crystals were grown from a saturated benzene solution at room temperature.

^1H NMR (benzene-d_6, 300.1 MHz, 293 K): 8.21 (1H, d, ^3J 5.0 Hz, 6-C_5H_4N), 7.33 (2H, d, ^4J 2.5 Hz, 4-$C_6H_2{}^tBu_2$), 6.89 (2H, d, ^4J 2.5 Hz, 6-$C_6H_2{}^tBu_2$), 6.35 (1H, app. td, app. ^3J 7.5 Hz, app. ^4J 1.5 Hz, 4-C_5H_4N), 6.15 (1H, app. t, app. ^3J 6.5 Hz, 5-C_5H_4N), 5.74 (1H, d, ^3J 7.5 Hz, 3-C_5H_4N), 4.20 (2H, d, ^2J 13.0 Hz, NCH_2Ar distal to C_5H_4N), 3.84 (6H, s, NMe_2 *cis* to C_5H_4N), 3.53 (6H, s, NMe_2 *trans* to C_5H_4N), 3.14 (2H, s, $NCH_2C_5H_4N$), 2.86 (2H, d, ^2J 13.0 Hz, NCH_2Ar proximal to C_5H_4N), 1.63 (18H, s, 3-$C_6H_2{}^tBu_2$), 1.34 (18H, s, 5-$C_6H_2{}^tBu_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 160.9 (2-$C_6H_2{}^tBu_2$), 157.9 (2-C_5H_4N), 149.5 (6-C_5H_4N), 138.7 (5-$C_6H_2{}^tBu_2$), 136.6 (4-C_5H_4N), 135.8 (3-$C_6H_2{}^tBu_2$), 124.6 (1-$C_6H_2{}^tBu_2$ or 6-$C_6H_2{}^tBu_2$), 124.5 (1-$C_6H_2{}^tBu_2$ or 6-$C_6H_2{}^tBu_2$), 123.4 (4-$C_6H_2{}^tBu_2$), 121.3 (5-C_5H_4N), 120.6 (3-C_5H_4N), 64.8 (NCH_2Ar), 58.6 ($NCH_2C_5H_4N$), 50.1 (NMe_2 *trans* to C_5H_4N), 49.3 (NMe_2 *cis* to C_5H_4N), 35.6 (3-$C_6H_2(CMe_3)_2$), 34.4 (5-$C_6H_2(CMe_3)_2$), 32.3 (5-$C_6H_2(CMe_3)_2$), 30.6 (3-$C_6H_2(CMe_3)_2$). IR (KBr plates, Nujol mull, cm^{-1}): 2803 (s), 2757 (s), 2360 (m), 2342 (m), 1605 (m), 1559 (w), 1542 (w), 1522 (w), 1508 (w), 1413 (s), 1377 (s), 1362 (m), 1340 (w), 1318 (m), 1302 (m), 1238 (s), 1207 (m), 1170 (m), 1151 (w), 1138 (m), 1075 (w), 1054 (m), 1017 (m), 978 (m), 961 (s), 947 (s), 916 (m), 903 (w), 878 (m), 870 (w), 838 (s), 771 (w), 759 (s). EIMS: *m/z* 678 (7%), $[M]^+$. Anal. Found (calcd for $C_{40}H_{62}N_4O_2Ti$): C, 70.8 (70.8); H, 9.2 (9.2); N, 8.2 (8.3).

$Ti(O_2{}^{Me}NN')(NMe_2)_2$ (12). To a stirred yellow solution of $Ti(NMe_2)_4$ (1.001 g, 4.46 mmol) in benzene (25 mL), cooled to 7 °C, was added dropwise a solution of $H_2O_2{}^{Me}NN'$ (1.681 g, 4.46 mmol) in benzene (20 mL). The solution was allowed to warm to room temperature and was stirred for 90 min, after which time the volatiles were removed under reduced pressure to give **12** as a rusty-orange powder. The product was washed with pentane (20 mL) and dried in vacuo. Yield: 1.54 g (79%).

^1H NMR (benzene-d_6, 300.1 MHz, 293 K): 8.40 (1H, app. dt, ^3J 4.5 Hz, app. ^4J 1.0 Hz, 6-C_5H_4N), 6.74 (2H, d, ^4J 2.0 Hz, 4-$C_6H_2Me_2$), 6.59 (2H, d, ^4J 2.0 Hz, 6-$C_6H_2Me_2$), 6.78 (1H, app. td, app. ^3J 7.5 Hz, ^4J 2.0 Hz, 4-C_5H_4N), 6.15 (1H, app. td, app. ^3J 6.5 Hz, ^4J 1.0 Hz 5-C_5H_4N), 5.64 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 4.30 (2H, d, ^2J 12.5 Hz, NCH_2Ar distal to C_5H_4N), 3.96 (6H, s, NMe_2 *cis* to C_5H_4N), 3.59 (6H, s, NMe_2 *trans* to C_5H_4N), 3.18 (2H, s, $NCH_2C_5H_4N$), 2.85 (2H, d, ^2J 12.5 Hz, NCH_2Ar proximal to C_5H_4N), 2.31 (6H, s, 3-$C_6H_2Me_2$), 2.21 (6H, s, 5-$C_6H_2Me_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 160.7 (2-$C_6H_2Me_2$), 157.7 (2-C_5H_4N), 148.8 (6-C_5H_4N), 136.8 (4-C_5H_4N), 131.3 (4-$C_6H_2Me_2$), 127.9 (6-$C_6H_2Me_2$), 125.5 (5-$C_6H_2Me_2$), 124.7 (3-$C_6H_2Me_2$), 123.9 (1-$C_6H_2Me_2$), 121.6 (5-C_5H_4N), 120.1 (3-C_5H_4N), 63.9 (NCH_2Ar), 58.5 ($NCH_2C_5H_4N$), 49.9 (NMe_2 *trans* to C_5H_4N), 48.6 (NMe_2 *cis* to C_5H_4N), 20.7 (5-$C_6H_2Me_2$), 17.4 (3-$C_6H_2Me_2$). IR (KBr plates, Nujol mull, cm^{-1}): 2755 (s), 2739 (s), 1603 (s), 1572 (w), 1456 (bs), 1411 (w), 1342 (s), 1319 (s), 1311 (w), 1299 (bs), 1241(w), 1220 (w), 1206 (w), 1159 (m), 1149 (m), 1114 (w), 1101 (w), 964 (s), 949 (s), 901 (w), 887 (w), 857 (m), 844 (m), 832 (s), 821 (s), 766 (w), 757 (m), 748 (w), 729 (m), 682 (w), 643 (m), 627 (m), 588 MB), 558 (s). EIMS: *m/z* 422 (100%), $[M - 2NMe_2]^+$. Anal. Found (calcd for $C_{28}H_{38}N_4O_2Ti$): C, 65.9 (65.9); H, 7.3 (7.5); N, 10.6 (11.0).

$Ti(O_2{}^{tBu}NN')(NMe_2)(S\text{-}4\text{-}C_6H_4Me)$ (13). To a stirred solution of $Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (**11**) (0.200 g, 0.295 mmol) in benzene (20 mL), cooled to 7 °C, was added dropwise a solution of $HS\text{-}4\text{-}C_6H_4Me$ (0.037 g, 0.295 mmol) in benzene (15 mL). The solution was allowed to warm to room temperature and then stirred for a further 90 min, after which time the volatiles were removed under reduced pressure to give crude **13** as an orange-brown powder. This was washed with pentane (35 mL) to give a yellow-brown powder, which was dried in vacuo to yield **13**. Yield: 0.116 g (52%).

^1H NMR (benzene-d_6, 300.1 MHz, 293 K): 9.22 (1H, d, ^3J 5.5 Hz, 6-C_5H_4N), 8.05 (2H, d, ^3J 8.0 Hz, *o*-SC_6H_4Me), 7.38 (2H, d, ^4J 2.5 Hz, 4-$C_6H_2{}^tBu_2$), 7.08 (2H, d, ^3J 8.0 Hz, *p*-SC_6H_4Me), 6.97 (2H, d, ^4J 2.5 Hz, 6-$C_6H_2{}^tBu_2$), 6.33 (1H, app. td, app. ^3J 7.5 Hz, ^4J 2.0 Hz, 4-C_5H_4N), 6.17 (1H, app. t, app. ^3J 7.5 Hz, 5-C_5H_4N), 5.57 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.93 (2H, d, ^2J 12.5 Hz, NCH_2Ar distal to C_5H_4N), 3.36 (6H, s, NMe_2), 3.10 (2H, s, $NCH_2C_5H_4N$), 2.88 (2H, d, ^2J 12.5 Hz, NCH_2Ar proximal to C_5H_4N), 2.16 (3H, s, SC_6H_4Me), 1.68 (18H, s, 3-$C_6H_2{}^tBu_2$), 1.32 (18H, s, 5-$C_6H_2{}^tBu_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 159.6 (2-$C_6H_2{}^tBu_2$), 157.2 (2-C_5H_4N), 150.6 (6-C_5H_4N), 143.6 (*i*-SC_6H_4Me), 140.2 (*p*-SC_6H_4Me), 137.0 (5-$C_6H_2{}^tBu_2$), 136.8 (4-C_5H_4N), 133.7 (*o*-SC_6H_4Me), 132.3 (3-$C_6H_2{}^tBu_2$), 128.2 (*o*-SC_6H_4Me), 124.9 (6-$C_6H_2{}^tBu_2$), 124.5 (1-$C_6H_2{}^tBu_2$), 124.1 (4-$C_6H_2{}^tBu_2$), 121.6 (5-C_5H_4N), 119.6 (3-C_5H_4N), 65.7 (NCH_2Ar), 58.3 ($NCH_2C_5H_4N$), 52.7 (NMe_2), 36.2 (3-$C_6H_2(CMe_3)_2$), 35.0 (5-$C_6H_2(CMe_3)_2$), 32.7 (5-$C_6H_2(CMe_3)_2$), 31.1 (3-$C_6H_2(CMe_3)_2$), 21.9 (SC_6H_4Me). IR (NaCl plates, Nujol mull, cm^{-1}): 1891 (w), 1869 (w), 1845 (w), 1830 (w), 1793 (w), 1772 (w), 1749 (w), 1734 (w), 1717 (w), 1699 (w), 1684 (w), 1670 (w), 1647 (w), 1636 (w), 1604 (m), 1569 (m), 1559 (w), 1541 (w), 1522 (w), 1507 (w), 1416 (m), 1365 (s), 1306 (s), 1287 (s), 1241 (s), 1203 (m), 1171 (s), 1131 (w), 1055 (w), 1040 (w), 1017 (m), 977 (w), 959 (s), 934 (w), 916 (w), 890 (m), 879 (w), 869 (s), 847 (s), 757 (s), 644 (w), 632 (w), 595 (m). EIMS: *m/z* 713 (7%), $[M - NMe_2]^+$; *m/z* 634 (100%), $[M - SC_6H_4Me]^+$. Anal. Found (calcd for $C_{45}H_{63}N_3O_2STi$): C, 71.0 (71.3); H, 8.2 (8.4); N, 5.6 (5.5).

$Ti(O_2{}^{tBu}NN')Me_2$ (14). To a stirred slurry of $Ti(O_2{}^{tBu}NN')Cl_2$ (0.750 g, 1.134 mmol) in benzene (30 mL), cooled to 7 °C, was added dropwise and in the absence of light a solution of MeMgBr (1.4 M in toluene/THF, 75:25, 1.62 mL, 2.268 mmol). The solution was allowed to warm to room temperature and then stirred for 1 h, after which time dioxane (5 mL) was added to encourage precipitation of magnesium halide salt products. After stirring for a further 5 min the volatiles were removed under reduced pressure. The residue was extracted into pentane (2 × 25 mL), filtered, and concentrated to give **14** as an off-yellow powder. Yield: 0.256 g (36%).

^1H NMR (benzene-d_6, 300.1 MHz, 293 K): 7.84 (1H, d, ^3J 8.0 Hz, 6-C_5H_4N), 7.43 (2H, d, ^4J 3.0 Hz, 4-$C_6H_2{}^tBu_2$), 6.88 (2H, d, ^4J 3.0 Hz, 6-$C_6H_2{}^tBu_2$), 6.31 (1H, app. td, app. ^3J 7.0 Hz, ^4J 1.5 Hz, 4-C_5H_4N), 6.04 (1H, app. t, app. ^3J 5.5 Hz, 5-C_5H_4N), 5.58 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.76 (2H, d, ^2J 13.0 Hz, NCH_2Ar distal to C_5H_4N), 2.93 (2H, s, $NCH_2C_5H_4N$), 2.64 (2H, d, ^2J 13.0 Hz, NCH_2Ar proximal to C_5H_4N), 1.97 (3H, s, Ti-Me *cis* to C_5H_4N), 1.83 (18H, s, 3-$C_6H_2{}^tBu_2$), 1.57 (3H, s, Ti-Me *trans* to C_5H_4N), 1.40 (18H, s, 5-$C_6H_2{}^tBu_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 160.9 (2-$C_6H_2{}^tBu$), 157.8 (2-C_5H_4N), 148.4 (6-C_5H_4N), 140.3 (5-$C_6H_2{}^tBu_2$), 136.9 (4-C_5H_4N), 135.9 (3-$C_6H_2{}^tBu_2$), 125.6 (1-$C_6H_2{}^tBu_2$), 124.8 (6-$C_6H_2{}^tBu_2$), 124.0 (4-$C_6H_2{}^tBu_2$), 121.4 (5-C_5H_4N), 120.1 (3-C_5H_4N), 63.7 (NCH_2Ar and Ti-Me *cis* to C_5H_4N), 61.9 (Ti-Me *trans* to C_5H_4N), 58.9 ($NCH_2C_5H_4N$), 35.9 (3-$C_6H_2(CMe_3)_2$), 34.7 (5-$C_6H_2(CMe_3)_2$), 32.4 (5-$C_6H_2(CMe_3)_2$), 30.7 (3-$C_6H_2(CMe_3)_2$). IR (NaCl plates, Nujol mull, cm^{-1}): 1732 (bw), 1603 (s), 1568 (w), 1414 (s), 1362 (m), 1304 (m), 1287 (s), 1239 (s), 1203 (s), 1169 (w), 1129 (w), 1155 (w), 1025 (w), 1012 (w) 977 (w), 931 (w), 915 (m), 882 (m), 857 (s), 847 (s), 772 (w), 760 (s), 725 (m), 629 (w), 598 (w). EI-HRMS: *m/z* found (calcd for $C_{37}H_{53}N_2O_2Ti$, $[M - Me]^+$) 605.3586 (605.3587). Anal. Found (calcd for $C_{38}H_{56}N_2O_2Ti$): C, 72.6 (73.5); H, 8.8 (9.1); N, 4.2 (4.5) (the low %C is attributed to titanium carbide formation).

$Ti(O_2{}^{Me}NN')Me_2$ (15). To a stirred slurry of $Ti(O_2{}^{Me}NN')Cl_2$ (0.75 g, 1.44 mmol) in toluene (30 mL), cooled to −78 °C, was added dropwise and in the absence of light a solution of MeMgBr (1.4 M in toluene/THF, 75:25, 2.06 mL, 2.88 mmol) in toluene (10 mL). The solution was allowed to warm to room temperature and stirred for a further 30 min, after which time dioxane (5 mL) was added. After stirring for a further 5 min the volatiles were removed under reduced pressure. The residue was extracted into diethyl ether (2 × 25 mL) and filtered. This solution was reduced to 10 mL, and hexanes (20 mL) were added. Cooling to −80 °C produced a yellow microcrystalline powder, which was dried in vacuo to give $Ti(O_2{}^{Me}NN')Me_2 \cdot nEt_2O$ ($\mathbf{11} \cdot n Et_2O$) (typical value of $n = 0.1$). Yield: 0.221 g (33%). The Et_2O content was determined by careful integration of the ^1H NMR spectrum.

^1H NMR (benzene-d_6, 300.1 MHz, 293 K): 7.96 (1H, d, ^3J 5.0 Hz, 6-C_5H_4N), 6.78 (2H, s, 4-$C_6H_2Me_2$), 6.52 (2H, s, 6-$C_6H_2Me_2$), 6.36 (1H, app. td, a ^3J 7.5 Hz, app. ^4J 1.5 Hz, 4-C_5H_4N), 6.05 (1H, app. t, app. ^3J 6.0 Hz, 5-C_5H_4N), 5.63 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.72 (2H, d, ^2J 12.5 Hz, NCH_2Ar distal to C_5H_4N), 3.00 (2H, s, $NCH_2C_5H_4N$), 2.69 (2H, d, ^2J 12.5 Hz, NCH_2Ar proximal to C_5H_4N), 2.51 (6H, s, 3-$C_6H_2Me_2$), 2.12 (6H, s, 5-$C_6H_2Me_2$), 1.90 (3H, s, Ti-Me *cis* to C_5H_4N), 1.52 (3H, s, Ti-Me *trans* to C_5H_4N). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 160.8 (2-$C_6H_2Me_2$), 157.7 (2-C_5H_4N), 147.4 (6-C_5H_4N), 136.8 (4-C_5H_4N), 131.6 (4-$C_6H_2Me_2$), 127.7 (6-$C_6H_2Me_2$), 126.9 (5-$C_6H_2Me_2$), 125.1 (3-$C_6H_2Me_2$), 124.3 (1-$C_6H_2Me_2$), 121.8 (5-C_5H_4N), 120.2 (3-C_5H_4N), 62.6 (NCH_2Ar), 61.4 (Ti-Me *trans* to C_5H_4N), 59.9 (Ti-Me *cis* to C_5H_4N), 59.5 ($NCH_2C_5H_4N$), 20.8 (5-$C_6H_2Me_2$), 16.6 (3-$C_6H_2Me_2$). IR (NaCl plates, Nujol mull, cm^{-1}): 1606 (m), 1571 (w), 1316 (m), 1305 (s), 1279 (m), 1155 (m), 1056 (s), 1038 (w), 1016 (s), 977 (w), 963 (w), 955 (m), 937 (m), 901 (w), 884 (w), 869 (m), 851 (m), 835 (s), 762 (w), 750 (m), 677 (m), 642 (w), 627 (m), 609 (s). EIMS: *m/z* 420 (43%), $[M - 2Me, - 2H]^+$. Anal. Found (calcd for $C_{26}H_{32}N_2O_2Ti \cdot 0.1(OEt_2)$): C, 68.7, (69.0); H, 7.6, (7.3); N, 6.0, (6.1).

$Ti(O_2{}^{tBu}NN')(N^tBu)(py)$ (16). To a stirred solution of $Ti(N^tBu)Cl_2(py)_3$ (0.726 g, 1.70 mmol) in pyridine (25 mL), cooled to 7 °C, was added dropwise a solution of $Na_2O_2{}^{tBu}NN'$ (1.00 g, 1.70 mmol) in pyridine (30 mL). The solution was heated to 80 °C for 2 h, after which time it was allowed to cool to room temperature. The volatiles were removed under reduced pressure to give a peach-colored solid. This was extracted into benzene (100 mL), the volume was reduced to 35 mL, and pentane (75 mL) was added. Cooling to −30 °C for 16 h produced a pale peach precipitate, which was washed with cold pentane (2 × 25 mL) and dried in vacuo to give **16**. Yield: 0.603 g (48%). Diffraction-quality crystals were grown from a saturated benzene solution at room temperature.

^1H NMR (benzene-d_6, 300 MHz, 293 K): 9.48 (3H, overlapping 2 × d, app. ^3J 4.4 Hz, 6-C_5H_4N and 2-C_5H_5N), 7.47 (2H, d, ^4J 2.5 Hz, 4-$C_6H_2{}^tBu_2$), 6.92 (2H, d, ^4J 2.5 Hz, 6-$C_6H_2{}^tBu_2$), 6.83 (1H, app. t, app. ^3J 6.5 Hz, 4-C_5H_5N), 6.55 (2H, app. t, app. ^3J 6.5 Hz, 3-C_5H_5N), 6.42 (1H, td, ^3J 8.0 Hz, ^4J 1.5 Hz, 4-C_5H_4N), 6.34 (1H, app. t, app. ^3J 6.5 Hz, 5-C_5H_4N), 5.66 (1H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.59 (2H, d, ^2J 12.0 Hz, NCH_2Ar distal to C_5H_4N), 3.17 (2H, s, $NCH_2C_5H_4N$), 2.62 (2H, d, ^2J 12.0 Hz, NCH_2Ar proximal to C_5H_4N), 1.95 (18H, s, 3-$C_6H_2{}^tBu_2$), 1.42 (18H, s, 5-$C_6H_2{}^tBu_2$), 1.39 (9H, s, N^tBu). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 162.6 (2-$C_6H_2{}^tBu_2$), 158.3 (2-C_5H_4N), 154.2 (2-C_5H_5N), 151.4 (6-C_5H_4N), 137.6 (5-$C_6H_2{}^tBu_2$), 137.0 (4-C_5H_4N), 136.9 (3-$C_6H_2{}^tBu_2$), 124.9 (6-$C_6H_2{}^tBu_2$), 124.0 (3-C_5H_5N), 123.6 (4-$C_6H_2{}^tBu_2$), 120.8 (5-C_5H_4N), 120.1 (3-C_5H_4N), 67.6 ($NCMe_3$), 63.9 (NCH_2Ar), 56.7 ($NCH_2C_5H_4N$), 36.3 (3 $C_6H_2(CMe_3)_2$), 34.6 (5 $C_6H_2(CMe_3)_2$), 33.0 ($NCMe_3$), 32.6 (5 $C_6H_2(CMe_3)_2$), 31.0 (3 $C_6H_2(CMe_3)_2$), 1-$C_6H_2{}^tBu_2$ and 4-C_5H_5N not observed, possibly obscured or overlapping with solvent or other compound resonances. IR (NaCl plates, Nujol mull, cm^{-1}): 1956 (w), 1870 (w), 1845 (w), 1773 (w), 1750 (w), 1734 (w), 1717 (w), 1699 (w), 1685 (w), 1670 (w), 1654 (w), 1646 (w), 1637 (w), 1606 (s), 1568 (m), 1541 (w), 1522 (w), 1416 (s), 1364 (s), 1346 (s), 1318 (s), 1304 (w), 1293 (s), 1240 (w), 1205 (m), 1168 (s), 1152 (w), 1132 (w), 1114 (m), 1104 (w), 1054 (w), 1038 (m), 1021 (w), 1011 (w), 976 (s), 947 (w), 934 (m), 914 (m), 895 (w), 880 (s), 842 (s), 799 (s), 780 (s), 764 (m), 749 (m), 703 (s), 679 (s), 647 (s). EIMS: *m/z* 590 (22%), $[M - N^tBu, - C_5H_5N]^+$. Anal. Found (calcd for $C_{45}H_{64}N_4O_2Ti$): C, 73.5 (73.0); H, 8.3 (8.7); N, 7.4 (7.6).

$Ti(O_2{}^{tBu}NN')(N\text{-}2,6\text{-}C_6H_3Me_2)(py)$ (17). To a stirred solution of $Ti(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(py)_3$ (0.807 g, 1.70 mmol) in pyridine (30 mL), cooled to 7 °C, was added dropwise a solution of $Na_2O_2{}^{tBu}NN'$ (1.00 g, 1.70 mmol) in pyridine (30 mL). The solution was heated to 80 °C for 2 h, after which time it was allowed to cool to room temperature. The volatiles were removed under reduced pressure to give an orange-brown solid, which was extracted in benzene (30 mL) and filtered. Pentane (25 mL) was added, and subsequent cooling to −30 °C for 4 days produced an orange-brown precipitate, from which the mother liquor was decanted. The orange-brown powder was washed with cold pentane (2 × 25 mL) and dried in vacuo to give **17**. Yield: 1.078 g (80%).

^1H NMR (benzene-d_6, 300.1 MHz, 293 K): 9.36 (2H, bs, 2-C_5H_5N), 9.19 (1H, d, ^3J 4.0 Hz, 6-C_5H_4N), 7.39 (2H, d, ^4J 2.5 Hz, 4-$C_6H_2{}^tBu_2$), 7.07 (2H, d, ^3J 7.5 Hz, *m*-$C_6H_3Me_2$), 6.80−6.65 (4H, overlapping m, 6-$C_6H_2{}^tBu_2$, *p*-$C_6H_3Me_2$ and 4-C_5H_5N), 6.50 (1H, td, ^3J 7.5 Hz, ^4J 2.0 Hz, 4-C_5H_4N), 6.42 (2H, app. t, app. ^3J 6.5 Hz, 3-C_5H_5N), 6.19 (1H, app. t, app. ^3J 7.0 Hz, 5-C_5H_4N), 5.83 (1H, d, ^3J 7.5 Hz, 3-C_5H_4N), 3.41 (2H, d, ^2J 12.5 Hz, NCH_2Ar distal to C_5H_4N), 3.12 (2H, s, $NCH_2C_5H_4N$), 2.68 (6H, s, N-2,6,-$C_6H_3Me_2$), 2.52 (2H, d, ^2J 13.0 Hz, NCH_2Ar proximal to C_5H_4N), 1.84 (18H, s, 3-$C_6H_2{}^tBu_2$), 1.36 (18H, s, 5-$C_6H_2{}^tBu_2$) $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz, 293 K): 162.6 (2-$C_6H_2{}^tBu_2$), 159.0 (*i*-$C_6H_3Me_2$), 158.4 (2-C_5H_4N), 153.4 (2-C_5H_5N), 151.0 (6-C_5H_4N), 137.9 (5-$C_6H_2{}^tBu_2$ and 4-C_5H_4N), 137.0 (3-$C_6H_2{}^tBu_2$), 131.7 (*o*-$C_6H_3Me_2$), 128.3 (*p*-$C_6H_3Me_2$), 127.9 (*m*-$C_6H_3Me_2$), 124.4 (6-$C_6H_2{}^tBu_2$ and 3-C_5H_5N), 123.4 (4-$C_6H_2{}^tBu_2$), 121.2 (3- and 5-C_5H_4N), 118.1 (4-C_5H_5N), 63.7 (NCH_2Ar), 57.8 ($NCH_2C_5H_4N$), 35.9 (3-$C_6H_2(CMe_3)_2$), 34.1 (5-$C_6H_2(CMe_3)_2$), 32.2 (5-$C_6H_2(CMe_3)_2$), 30.6 (3-$C_6H_2(CMe_3)_2$), 20.5 (N-2,6,-$C_6H_3Me_2$), 1-$C_6H_2{}^tBu_2$ not observed, possibly obscured or overlapping with solvent or other compound resonances. IR (NaCl plates, Nujol mull, cm^{-1}): 1606 (s), 1586 (w), 1570 (w), 1412 (m), 1284 (s), 1214 (s), 1203 (m), 1167 (s), 1155 (m), 1134 (m), 1117 (m), 1106 (w), 1070 (m), 1056 (m), 1041 (m), 1023 (s), 1014 (s), 977 (m), 954 (m), 936 (w), 914 (m), 889 (w), 873 (m), 847 (s), 837 (s), 764 (m), 756 (s), 702 (s), 679 (s), 648 (m), 635 (w). EIMS: *m/z* 679 (19%), $[M - C_5H_5N, - 2Me]^+$; *m/z* 590 (35%), $[M - C_5H_5N, - NC_6H_3Me_2]^+$. Anal. Found (calcd for $C_{49}H_{64}N_4O_2Ti$): C, 74.9 (74.6); H, 8.2 (8.2); N, 6.1 (7.1) (the low %N is attributed to titanium nitride formation as is well-known for imidotitanium compounds[42]).

Alternative NMR Tube Scale Synthesis of $Ti(O_2{}^{tBu}NN')(N\text{-}2,6\text{-}C_6H_3Me_2)(py)$ (17). To an orange-brown solution of $Ti(O_2{}^{tBu}NN')(N^tBu)(py)$ (**16**) (0.020 g, 0.027 mmol) in benzene-d_6 (0.75 mL) in a 5 mm J. Young NMR tube was added 2,6-dimethylaniline (0.0033 g, 0.027 mmol). After heating for 6 days at 80 °C an ^1H NMR spectrum confirmed that the reaction had proceeded quantitatively to give **17** and H_2N^tBu.

$Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2$ (18). To a stirred orange-brown solution of $Ti(O_2{}^{tBu}NN')(N^tBu)(py)$ (**16**) (0.200 g, 0.270 mmol) in benzene (20 mL) cooled to 7 °C was added dropwise a solution of water in THF (1.00 M, 0.270 mL, 0.270 mmol), further dispersed in benzene (15 mL). During the addition the solution turned lime green in color. It was subsequently allowed to warm to room temperature and stirred for a further 30 min. The volatiles were removed under reduced pressure to leave a pale yellow-green powder, which was recrystallized from dichloromethane/hexanes (5:10 mL) at −80 °C to give **18**. Yield: 0.057 g (33%). Diffraction-quality crystals were grown from a saturated dichloromethane solution at room temperature.

^1H NMR (dichloromethane-d_2, 300.1 MHz, 293 K): 8.66 (2H, d, ^3J 4.5 Hz, 6-C_5H_4N), 7.23 (2H, atd, a ^3J 7.5 Hz, a^4J 1.0 Hz, 4-C_5H_4N), 7.04 (2H, d, ^4J 2.0 Hz, 6-$C_6H_2{}^tBu_2$ (a)), 6.93 (2H, d, ^4J 2.0 Hz, 4-$C_6H_2{}^tBu_2$ (a)), 6.88 (2H, d, ^3J 8.0 Hz, 3-C_5H_4N), 6.72 (2H, at, a ^3J 7.0 Hz, 5-C_5H_4N), 6.67 (2H, d, ^4J 2.5 Hz, 6-$C_6H_2{}^tBu_2$ (b)), 6.49 (2H, d, ^4J 2.5 Hz, 4-$C_6H_2{}^tBu_2$ (b)), 4.79 (4H, m, NCH_2Ar (f) and $NCH_2C_5H_4N$), 3.58 (2H, d, ^2J 14.0 Hz, $NCH_2C_5H_4N$), 3.39 (2H, d, ^2J 13.0 Hz, NCH_2Ar (e)), 3.21 (2H, d, ^2J 12.0 Hz, NCH_2Ar (f)), 2.58 (2H, d, ^2J 13.0 Hz, NCH_2Ar (e)), 1.30 (18H, s, 3-$C_6H_2{}^tBu_2$ (b)), 1.23 (18H, s, 5-$C_6H_2{}^tBu_2$ (b)), 1.06 (18H, s, 3-$C_6H_2{}^tBu_2$ (a)), 0.91 (18H, s, 5-$C_6H_2{}^tBu_2$ (a)), the designations (a) and (b), (c) and (d), and (e) and (f) relate pairs of resonances to protons on specific phenoxy groups. However which group lies *cis*, and which *trans*, to the pyridyl group could not be determined. $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 75.5 MHz, 293 K): 161.2 (2-$C_6H_2{}^tBu_2$), 159.1 (2-$C_6H_2{}^tBu_2$), 156.6 (2-C_5H_4N), 151.6 (6-C_5H_4N), 139.7 (5-$C_6H_2{}^tBu_2$ (a)), 138.4 (5-$C_6H_2{}^tBu_2$ (b)), 137.9 (4-C_5H_4N), 136.1 (3-$C_6H_2{}^tBu_2$ (b)), 134.3 (3-$C_6H_2{}^tBu_2$ (a)), 126.0 (1-$C_6H_2{}^tBu_2$), 125.8 (1-$C_6H_2{}^tBu_2$), 124.8 (4-$C_6H_2{}^tBu_2$ (c)), 124.0 (4-$C_6H_2{}^tBu_2$ (d)), 123.7 (6-$C_6H_2{}^tBu_2$ (c)), 122.7 (5-C_5H_4N), 122.4 (6-$C_6H_2{}^tBu_2$ (d)), 121.4 (3-C_5H_4N), 64.0 ($NCH_2C_5H_4N$), 62.3 (NCH_2Ar (f)), 59.2 (NCH_2Ar (e)), 35.1 (3-$C_6H_2(CMe_3)_2$ (a or b)), 35.0 (3-$C_6H_2(CMe_3)_2$ (b or a)), 34.3 (5-$C_6H_2(CMe_3)_2$ (b)), 33.9 (5-$C_6H_2(CMe_3)_2$ (a)), 31.8 (5-$C_6H_2(CMe_3)_2$ (b)), 31.7 (5-$C_6H_2(CMe_3)_2$ (a)), 30.3 (3-$C_6H_2(CMe_3)_2$ (b)), 30.2 (3-$C_6H_2(CMe_3)_2$ (a)). IR (NaCl plates, Nujol mull, cm^{-1}): 1869 (w), 1845 (w), 1830 (w), 1793 (w), 1772 (w), 1749 (w), 1734 (w), 1717 (w), 1699 (w), 1684 (w), 1670 (w), 1654 (w), 1636 (w), 1609 (m), 1576 (w), 1559 (w), 1542 (w), 1522 (w), 1508 (w), 1414 (m), 1340 (w), 1325 (w), 1291 (m), 1277 (s), 1242 (s), 1203 (m), 1170 (s), 1153 (w), 1134 (m), 1100 (m), 1026 (s), 977 (m), 916 (w), 876 (m), 861 (w), 840 (s), 778 (s), 767 (vs), 755 (s), 747 (s), 724 (m), 699 (w), 649 (m). EIMS: *m/z* 1212 (4%), $[M]^+$; *m/z* 606 (49%), $[^1/_2\ M]^+$. Anal. Found (calcd for $C_{72}H_{100}N_4O_6Ti_2$): C, 71.2 (71.3); H, 8.5 (8.3); N, 4.5 (4.6).

NMR Tube Scale Reaction of $Ti(O_2{}^{tBu}NN')(N^tBu)(py)$ (16) with CO_2. A solution of $Ti(O_2{}^{tBu}NN')(N^tBu)(py)$ (**16**) (0.010 g, 0.014 mmol) in benzene-d_6 (0.75 mL) was transferred to a 5 mm J. Young NMR tube. The solution was degassed by three freeze−pump−thaw cycles before addition of CO_2 (1 atm) to the solution at room temperature. After 1 h, the ^1H NMR spectrum showed that the major products (>95% by integral) were **18** and ^tBuNCO.

NMR Tube Scale Reaction of $Ti(O_2{}^{tBu}NN')(N\text{-}2,6\text{-}C_6H_3Me_2)(py)$ (17) with CO_2. A solution of $Ti(O_2{}^{tBu}NN')(N\text{-}2,6\text{-}C_6H_3Me_2)(py)$ (**17**) (0.011 g, 0.014 mmol) in benzene-d_6 (0.75 mL) was transferred to a 5 mm J. Young NMR tube. The solution was degassed by three freeze−pump−thaw cycles before addition of CO_2 (1 atm) to the solution at room temperature. After 1 h, the ^1H NMR spectrum showed that the major products (>95%) were **18** and ArNCO (Ar = 2,6-$C_6H_3Me_2$).

$Ti(O_2{}^{tBu}N)(N^tBu)(py)$ (19). To a stirred solution of $Ti(N^tBu)Cl_2(py)_3$ (0.40 g, 0.93 mmol) in THF (20 mL) was added a stirred solution of $Na_2O_2{}^{tBu}N$ (0.50 g, 0.93 mmol) in THF (20 mL), and the resulting solution was stirred at 60 °C for 16 h. Volatiles were removed under reduced pressure and the residues extracted into pentane (30 mL) and cooled to −80 °C. The pale orange product **19** was washed with −80 °C pentane (10 mL) and dried in vacuo. Yield: 0.017 g, (3%).

Note: the compound exists as a mixture of two isomers formed in a ratio of 2:1. Only ^1H NMR characterization was carried out on this compound, which was obtained in small quantities. ^1H NMR (C_6D_6, 300.0 MHz, 293 K): 9.18 (2H, m, 2-C_5H_5N), 9.10 (2H, m, 2-C_5H_5N), 7.57 (4H, d, 4 and 6-$C_6H_2{}^tBu_2$) 2 overlapping, 7.23 (2H, d, ^4J 2.3 Hz, 4/6-$C_6H_2{}^tBu_2$), 7.05

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[42] See the following and references therein: Carmalt, C. J.; Newport, A.; Parkin, I. P.; Mountford, P.; Sealey, A. J.; Dubberley, S. R. *J. Mater. Chem.* **2003**, *13*, 84.

(2H, d, ^4J 2.9 Hz, 4/6-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$), 6.93 (2H, m, 4-$\mathrm{C_5}H_5\mathrm{N}$) 2 overlapping, 6.65 (4H, m, 3-$\mathrm{C_5}H_5\mathrm{N}$) 2 overlapping, 5.53 (2H, d, ^2J 13.5 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.97 (2H, d, ^2J 13.5 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.77 (2H, d, ^2J 14.0 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.62 (2H, d, ^2J 13.5 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.46 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.58 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 1.46 (20H, d, $\mathrm{C_6H_2}{}^tBu_2$ and $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.40 (20H, d, $\mathrm{C_6H_2}{}^tBu_2$ and $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.20 (9H, s, $\mathrm{N^tBu}$), 1.08 (9H, s, $\mathrm{N^tBu}$), 0.52 (3H, t, ^3J 7.0 Hz, $\mathrm{CH_2CH_2C}H_3$), 0.20 (3H, t, ^3J 7.0 Hz, $\mathrm{CH_2CH_2C}H_3$).

$\mathbf{Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)}$ (20). To a stirred solution of $\mathrm{Ti(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_2(py)_3}$ (0.81 g, 2.78 mmol) in THF (20 mL) was added a stirred solution of $\mathrm{Na_2O_2{}^{tBu}N}$ (1.50 g, 2.78 mmol) in THF (20 mL) and the resulting solution stirred under partial reduced pressure at 60 °C for 16 h. Volatiles were removed under reduced pressure and the residues extracted into pentane/dichloromethane (9:1 v/v; 30 mL) and cooled to −80 °C. The orange solid product **20** was washed with −80 °C pentane (10 mL) and dried in vacuo. Yield: 0.93 g (45%). Diffraction-quality crystals of **2** were grown from a saturated benzene solution.

Note: the compound exists as a mixture of two isomers formed in a ratio of 3:1. The actual ratio depends on the individual preparation. ^{1}H NMR ($\mathrm{C_6D_6}$, 300.0 MHz, 293 K): 8.80 (2H, m, 2-$\mathrm{C_5}H_5\mathrm{N}$), 8.76 (2H, m, 2-$\mathrm{C_5}H_5\mathrm{N}$), 7.56 (4H, d, 4 and 6 $\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$) 2 overlapping doublets, 7.14 (2H, d, ^4J 2.3 Hz, 4-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$), 7.03 (4H, m, 6-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$ and 3-$\mathrm{C_6}H_3\mathrm{Me_2}$), 6.93 (2H, d, ^3J 7.6 Hz, 3-$\mathrm{C_6}H_3\mathrm{Me_2}$), 6.80 (2H, m, 4-$\mathrm{C_5}H_5\mathrm{N}$) 2 overlapping, 6.71 (2H, m, 4-$\mathrm{C_6}H_3\mathrm{Me_2}$) 2 overlapping, 6.45 (4H, m, 3-$\mathrm{C_5}H_5\mathrm{N}$) 2 overlapping, 5.11 (2H, d, ^2J 14.1 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 4.03 (2H, d, ^2J 13.5 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.74 (2H, d, ^2J 14.1 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.62 (2H, d, ^2J 14.1 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.27 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.77 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.73 (6H, s, 2-N-2.6-$\mathrm{C_6H_3}Me_2$), 2.52 (6H, s, 2-N-2,6-$\mathrm{C_6H_3}Me_2$), 1.48 (38H, d, 3-$\mathrm{C_6H_2}{}^tBu_2$ and $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.42 (38H, d, 5-$\mathrm{C_6H_2}{}^tBu_2$ and $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 0.41 (3H, t, ^3J 7.6 Hz, $\mathrm{CH_2CH_2C}H_3$), 0.25 (3H, t, ^3J 7.6 Hz, $\mathrm{CH_2CH_2C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 75.5 MHz, 293 K): 160.7 (2-$C_6\mathrm{H_2{}^tBu_2}$), 160.6 (2-$C_6\mathrm{H_2{}^tBu_2}$), 159.1 (1-N-2,6-$C_6\mathrm{H_3Me_2}$) 2 overlapping, 150.6 (2-$C_5\mathrm{H_5N}$), 150.3 (2-$C_5\mathrm{H_5N}$), 139.2 (4-$C_5\mathrm{H_5N}$), 139.1 (4-$C_5\mathrm{H_5N}$), 139.0 (5-$C_6\mathrm{H_2{}^tBu_2}$) 2 overlapping, 136.2 (1-$C_6\mathrm{H_2{}^tBu_2}$), 136.1 (1-$C_6\mathrm{H_2{}^tBu_2}$), 133.7 (3-$C_6\mathrm{H_2{}^tBu_2}$), 133.2 (3-$C_6\mathrm{H_2{}^tBu_2}$), 125.0 (4/6-$C_6\mathrm{H_2{}^tBu_2}$), 124.5 (3-$C_5\mathrm{H_5N}$), 124.3 (3-$C_5\mathrm{H_5N}$), 124.2 (4/6-$C_6\mathrm{H_2{}^tBu_2}$), 123.5 (4/6-$C_6\mathrm{H_2{}^tBu_2}$), 123.2 (4/6-$C_6\mathrm{H_2{}^tBu_2}$), 120.9 (4-N-2,6-$C_6\mathrm{H_3Me_2}$) 2 overlapping, 60.4 ($C\mathrm{H_2C_6H_2{}^tBu_2}$), 58.2 ($C\mathrm{H_2CH_2CH_3}$), 50.8 ($C\mathrm{H_2C_6H_2{}^tBu_2}$), 48.8 ($C\mathrm{H_2CH_2CH_3}$), 35.1 (5-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 35.0 (5-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 34.4 (3-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 34.3 (3-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 32.1 (3-$\mathrm{C_6H_2}{}^tBu_2$ & 5-$\mathrm{C_6H_2}{}^tBu_2$), 30.1 (5-$\mathrm{C_6H_2}{}^tBu_2$), 29.9 (3-$\mathrm{C_6H_2}{}^tBu_2$), 20.1 (2-N-2,6-$\mathrm{C_6H_3}Me_2$), 19.3 (2-N-2,6-$\mathrm{C_6H_3}Me_2$), 14.9 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 13.5 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 11.5 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$), 11.3 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$). Note: (2-N-2,6-$C_6\mathrm{H_3Me_2}$) 2 overlapping and (3-N-2,6-$C_6\mathrm{H_3Me_2}$) 2 overlapping, both obscured by the solvent resonance. IR (KBr pellet, cm^{-1}): 12952 (s), 2902 (s), 2868 (m), 1604 (m), 1476 (s), 1444 (s), 1412 (m), 1392 (w), 1266 (s), 1240 (s), 1204 (m), 1170 (m), 1132 (w), 1092 (w), 1042 (w), 916 (w), 848 (s), 756 (s), 698 (m), 638 (w), 620 (w), 472 (w). EIMS: *m*/*z* 660 (60%), [M − py]$^+$. Anal. Found (calcd for $\mathrm{C_{46}H_{65}N_3O_2Ti\cdot 0.1(CH_2Cl_2)}$): C 74.0 (74.0), H 8.9 (8.8), N 5.4 (5.6).

$\mathbf{Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(py)}$ (21). To a stirred solution of $\mathrm{Ti(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(py)_3}$ (0.59 g, 1.11 mmol) in THF (20 mL) was added a stirred solution of $\mathrm{Na_2O_2{}^{tBu}N}$ (0.60 g, 1.11 mmol) in THF (20 mL) and the resulting solution stirred under partial reduced pressure at 60 °C for 16 h. Volatiles were removed under reduced pressure and the residues extracted into pentane/dichloromethane (9:1 v/v; 30 mL) and cooled to −80 °C. The pale orange product **21** was washed with −80 °C pentane (10 mL) and dried in vacuo. Yield: 0.18 g (21%). A small quantity of diffraction-quality crystals of **21** was also isolated from this reaction.

Note: the compound exists as a mixture of two isomers formed in a ratio of 3:2. ^{1}H NMR ($\mathrm{C_6D_6}$, 300.0 MHz, 293 K): 8.84 (2H, m, 2-$\mathrm{C_5}H_5\mathrm{N}$), 8.80 (2H, m, 2-$\mathrm{C_5}H_5\mathrm{N}$), 7.54 (4H, m, 4- and 6-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$) 2 overlapping doublets, 7.12 (2H, d, ^4J 2.9 Hz 4/6-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$), 7.08 (4H, m, 3-N-2,6-$\mathrm{C_6}H_3{}^\mathrm{i}\mathrm{Pr_2}$) 2 overlapping, 7.05 (2H, d, ^4J 2.9 Hz, 4/6-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$), 6.88 (4H, m, 4-N-2,6-$\mathrm{C_6}H_3{}^\mathrm{i}\mathrm{Pr_2}$ and 4-$\mathrm{C_5}H_5\mathrm{N}$), 6.56 (2H, m, 3-$\mathrm{C_5}H_5\mathrm{N}$), 6.48 (2H, m, 3-$\mathrm{C_5}H_5\mathrm{N}$), 4.94 (2H, d, $^2J = 14.7$ Hz $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 4.76 (1H, sep, 2-N-2,6-$\mathrm{C_6H_3(}H{}^\mathrm{i}\mathrm{Pr_2}$), 4.46 (1H, sep, 2-N-2,6-$\mathrm{C_6H_3(}H{}^\mathrm{i}\mathrm{Pr_2}$), 4.10 (2H, d, ^2J 14.7 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.85 (2H, d, ^2J 14.7 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.65 (2H, d, ^2J 14.7 Hz, $\mathrm{C}H_2\mathrm{C_6H_2{}^tBu_2}$), 3.27 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.87 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 1.47 (36H, d, 3-$\mathrm{C_6H_2}{}^tBu_2$), 1.42 (36H, d, 5-$\mathrm{C_6H_2}{}^tBu_2$), 1.31 (16H, m, 2-N-2,6-$\mathrm{C_6H_3}{}^iPr_2$ and $\mathrm{CH_2C}H_2\mathrm{CH_3}$) 2 overlapping, 1.12 (12H, m, 2-N-2,6-$\mathrm{C_6H_3}{}^iPr_2$), 0.42 (3H, t, ^3J 7.1 Hz, $\mathrm{CH_2CH_2C}H_3$), 0.24 (3H, t, ^3J 7.1 Hz, $\mathrm{CH_2CH_2C}H_3$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 75.5 MHz, 293 K): 160.4 (2-$C_6\mathrm{H_2{}^tBu_2}$), 160.3 (2-$C_6\mathrm{H_2{}^tBu_2}$), 156.3 (1-N-2,6-$C_6\mathrm{H_3{}^iPr_2}$), 155.7 (1-N-2,6-$C_6\mathrm{H_3{}^iPr_2}$), 150.9 (2-$C_5\mathrm{H_5N}$), 150.3 (2-$C_5\mathrm{H_5N}$), 144.6 (5-$C_6\mathrm{H_2{}^tBu_2}$), 144.3 (5-$C_6\mathrm{H_2{}^tBu_2}$), 139.4 (4-$C_5\mathrm{H_5N}$), 139.2 (4-$C_5\mathrm{H_5N}$), 139.0 (1-$C_6\mathrm{H_2{}^tBu_2}$) 2 overlapping, 136.3 (3-$C_6\mathrm{H_2{}^tBu_2}$) 2 overlapping, 124.8 (3-$C_5\mathrm{H_5N}$) 2 overlapping, 124.4 (4/6-$C_6\mathrm{H_2{}^tBu_2}$), 124.3 (4/6-$C_6\mathrm{H_2{}^tBu_2}$), 124.2 (4/6-$C_6\mathrm{H_2{}^tBu_2}$), 123.4 (4-N-2,6-$C_6\mathrm{H_3{}^iPr_2}$), 123.1 (4-N-2,6-$C_6\mathrm{H_3{}^iPr_2}$), 60.4 ($C\mathrm{H_2C_6H_2{}^tBu_2}$), 58,2 ($C\mathrm{H_2CH_2CH_3}$), 58.1 ($C\mathrm{H_2C_6H_2{}^tBu_2}$), 49.4 ($C\mathrm{H_2CH_2CH_3}$), 35.1 (3-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 35.0 (5-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 34.4 (5-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 34.3 (3-$\mathrm{C_6H_2(}C\mathrm{Me_3)_2}$), 32.0 (3-$\mathrm{C_6H_2}{}^tBu_2$) 2 overlapping, 30.1 (5-$\mathrm{C_6H_2}{}^tBu_2$), 29.9 (5-$\mathrm{C_6H_2}{}^tBu_2$), 27.4 (2-N-2,6-$\mathrm{C_6H_3(}C{}^\mathrm{i}\mathrm{Pr_2)}$), 27.1 (2-N-2,6-$\mathrm{C_6H_3(}C{}^\mathrm{i}\mathrm{Pr_2)}$), 24.6 (2-N-2,6-$\mathrm{C_6H_3}{}^iPr_2$) 2 overlapping, 15.0 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 13.4 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 11.7 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$), 11.3 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$). Note: 4/6-$C_6\mathrm{H^tBu_2}$, 3-N-2,6-$C_6\mathrm{H_3{}^iPr_2}$ (2 overlapping), and 2-N-2,6-$C_6\mathrm{H_3{}^iPr_2}$ (2 overlapping) all obscured by solvent resonance. IR (KBr pellet, cm^{-1}): 2956 (s), 2904 (s), 2866 (s), 2708 (w), 1606 (m), 1582 (w), 1476 (s), 1446 (s), 1360 (m), 1338 (s), 1238 (m), 1216 (m), 1098 (w), 1044 (m), 1016 (w), 988 (m), 844 (s), 806 (m), 754 (s), 640 (m), 570 (s), 546 (w), 514 (s). EIMS: *m*/*z* 542 (8%), [M − py − NAr]$^+$.

NMR Tube Scale Reaction of $\mathbf{Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)}$ (20) with $\mathbf{CO_2}$. A solution of $\mathrm{Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)}$ (**20**) (10 mg, 0.013 mmol) in benzene-d_6 was exposed to $\mathrm{CO_2}$ at a pressure of 1.02 atm via a Schlenk line. The reaction was monitored using ^{1}H NMR spectroscopy over a period of 48 h. A red solid precipitated out of the orange solution during this time and was analyzed by ^{1}H NMR spectroscopy (dichloromethane-d_2). The spectrum showed a series of unidentifiable peaks, none of which correspond to the desired product. Attempts to obtain a clean product on scale-up were equally unsuccessful.

$\mathbf{[Ti_2(O_2{}^{tBu}NN')_2Me_2]\cdot 2[MeB(Ar^F)_3]}$ (22-$\mathbf{[MeB(Ar^F)_3]}$). To a stirred solution of $\mathrm{Ti(O_2{}^{tBu}NN')Me_2}$ (**14**) (0.200 g, 0.323 mmol) in dichloromethane (20 mL) cooled to −78 °C was added dropwise a solution of $\mathrm{B(Ar^F)_3}$ (0.165 g, 0.323 mmol) in dichloromethane (5 mL). The resulting orange-red solution was allowed to stir for a further 15 min at −78 °C before warming to 0 °C. The solution was concentrated to 5 mL, and hexanes (10 mL) were added. After cooling to −78 °C for 2 h a red oil separated. The supernatant was decanted away and the oil washed with hexanes (3 × 10 mL) and dried in vacuo to give **22**-$\mathrm{[MeB(Ar^F)_3]}$ as a red solid. Yield: 0.332 g (91%).

^{1}H NMR (dichloromethane-d_2, 500.0 MHz, 183 K): 8.71 (2H, s, 6-$\mathrm{C_5H_4N}$), 8.21 (2H, app. t, app. ^3J 7.0 Hz, 4-$\mathrm{C_5H_4N}$), 7.70 (2H, br s, 5-$\mathrm{C_5H_4N}$), 7.65 (2H, d, ^3J 7.0 Hz, 3-$\mathrm{C_5H_4N}$), 7.24 (2H, s, 4-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$ (a)), 7.22 (2H, s, 4-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$ (b)), 7.08 (2H, s, 6-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$ (b)), 7.04 (2H, s, 6-$\mathrm{C_6}H_2{}^\mathrm{t}\mathrm{Bu_2}$ (a)), 4.57 (2H, d, ^2J 16.5 Hz, $\mathrm{NC}H_2\mathrm{Ar}$ (a or b)), 4.36 (2H, d, ^2J 13.5 Hz, $\mathrm{NC}H_2\mathrm{C_5H_4N}$), 3.81 (4H, overlapping d, app. ^2J 15.0 Hz, $\mathrm{NC}H_2\mathrm{Ar}$ (a and b)), 3.52−3.42 (4H, overlapping m, app. ^3J 12.0 Hz, $\mathrm{NC}H_2\mathrm{C_5H_4N}$ and $\mathrm{NC}H_2\mathrm{Ar}$ (a or b)), 2.24 (6H, s, Ti-*Me*), 1.35 (36H, overlapping s, 3-$\mathrm{C_6H_2}{}^tBu_2$ (a and b)), 1.14 (18H, s, 5-$\mathrm{C_6H_2}{}^tBu_2$ (a or b)), 1.10 (18H, s, 5-$\mathrm{C_6H_2}{}^tBu_2$ (a or b)), 0.28 (6H, s, $\mathrm{(C_6F_5)_3B}Me$). The designations (a) and (b) relate resonances to protons on a specific phenoxy group. However, which group lies *cis*, and which *trans*, to the pyridyl group could not be determined. ^{13}C{^{1}H} NMR (dichloromethane-d_2, 125.7 MHz, 183 K): 159.8 (2-

Table 11. X-ray Data Collection and Processing Parameters for $Sc(O_2{}^{tBu}NN')Cl(py)\cdot C_6H_6$ ($2\cdot C_6H_6$), $Sc_2(O_2{}^{Me}NN')_2Cl_2\cdot 2CH_2Cl_2$ ($3\cdot 2CH_2Cl_2$), $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2\cdot 3(C_6H_6)$ ($4\cdot 3C_6H_6$), $Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (11), $Ti(O_2{}^{tBu}NN')Cl_2\cdot 0.5CH_2Cl_2$ ($9\cdot 0.5CH_2Cl_2$), $Ti(O_2{}^{Me}NN')Cl_2\cdot 2.5C_6H_6$ ($10\cdot 2.5C_6H_6$), $Ti(O_2{}^{tBu}NN')(N^{tBu})(py)\cdot 2C_6H_6$ ($16\cdot 2C_6H_6$), $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2\cdot 3CH_2Cl_2$ ($18\cdot 3CH_2Cl_2$), $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)\cdot 0.5C_6H_6$ ($20\cdot 0.5C_6H_6$), and $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(py)$ (21)

	2·C_6H_6	**3**·$2CH_2Cl_2$	**4**·$3C_6H_6$	**9**·$0.5CH_2Cl_2$
empirical formula	$C_{41}H_{55}Cl_1N_3O_2Sc_1\cdot C_6H_6$	$C_{48}H_{52}Cl_2N_4O_4Sc_2\cdot 2(CH_2Cl_2)$	$C_{82}H_{110}Cl_2N_6O_4Y_2\cdot 3(C_6H_6)$	$C_{36}H_{50}Cl_2N_2O_2Ti\cdot 0.5(CH_2Cl_2)$
fw	780.43	1079.65	1726.88	704.08
temp/K	150	150	150	150
wavelength/Å	0.71073	0.71073	0.71073	0.71073
space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
a/Å	27.0551(8)	11.7034(1)	14.4214(3)	27.2581(5)
b/Å	17.8450(5)	12.0006(1)	17.2881(3)	13.1736(3)
c/Å	19.0419(8)	18.5464(2)	22.0078(6)	24.6155(7)
α/deg	90	89.9518(6)	107.2666(6)	90
β/deg	95.537(1)	84.0259(6)	106.5164(7)	122.040(1)
γ/deg	90	88.0933(5)	91.0214(8)	90
V/Å^3	9150.5(5)	2589.21(4)	4992.1(2)	7492.7(3)
Z	8	2	2	8
d(calcd)/Mg·m^{-3}	1.130	1.385	1.15	1.243
abs coeff/mm^{-1}	0.261	0.618	1.26	0.475
R indices R_1, R_w $[I > 3\sigma(I)]^a$	$R_1 = 0.0667$ $R_w = 0.0882$	$R_1 = 0.0387$ $R_w = 0.0398$	$R_1 = 0.0762$ $R_w = 0.0629$	$R_1 = 0.0698$ $R_w = 0.0842$

	10·$2.5C_6H_6$	**11**	**16**·$2C_6H_6$	**18**·$3CH_2Cl_2$
empirical formula	$C_{24}H_{26}Cl_2N_2O_2Ti\cdot 2.5(C_6H_6)$	$C_{40}H_{62}N_4O_2Ti$	$C_{45}H_{64}N_4O_2Ti\cdot 2(C_6H_6)$	$C_{72}H_{100}N_4O_6Ti_2\cdot 3(CH_2Cl_2)$
fw	688.57	678.86	897.16	1468.21
temp/K	150	150	150	150
wavelength/Å	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	15.7447(7)	10.1066(3)	10.9050(2)	13.4550(2)
b/Å	9.0987(4)	10.1244(3)	15.6222(3)	15.6131(2)
c/Å	24.792(2)	19.6020(8)	16.7849(4)	20.7997(3)
α/deg	90	104.228(1)	98.2396(7)	95.4649(5)
β/deg	92.451(2)	97.719(1)	106.5212(8)	96.8717(6
γ/deg	90	95.997(2)	102.9245(9)	113.9600(6)
V/Å^3	3548.4(4)	1906.8(1)	2605.6(1)	3914.1(1)
Z	4	2	2	2
d(calcd)/Mg·m^{-3}	1.29	1.18	1.14	1.246
abs coeff/mm^{-1}	0.42	0.26	0.21	0.459
R indices R_1, R_w $[I > 3\sigma(I)]^a$	$R_1 = 0.0581$ $R_w = 0.0641$	$R_1 = 0.0528$ $R_w = 0.0480$	$R_1 = 0.0668$ $R_w = 0.0725$	$R_1 = 0.0479$ $R_w = 0.0520$

	20·$0.5C_6H_6$	**21**
empirical formula	$C_{46}H_{79}N_3O_2Ti\cdot 0.5C_6H_6$	$C_{50}H_{73}N_3O_2Ti$
fw	783.03	796.05
temp/K	150	150
wavelength/Å	0.71073	0.71073
space group	$P2_1/c$	$P2_1/n$
a/Å	13.0792(2)	11.4403(2)
b/Å	34.8093(3)	16.7426(2)
c/Å	11.2256(2)	25.1924(3)
α/deg	90	90
β/deg	112.2147(4)	90.9770(6)
γ/deg	90	90
V/Å^3	4731.4(1)	4824.7(2)
Z	4	4
d(calcd)/Mg·m^{-3}	1.099	1.096
abs coeff/mm^{-1}	0.219	0.216
R indices R_1, R_w $[I > 3\sigma(I)]^a$	$R_1 = 0.0390$ $R_w = 0.0408$	$R_1 = 0.0415$ $R_w = 0.0489$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2)\}^{1/2}$.

$C_6H_2{}^tBu_2$ (a)), 159.3 (2-C_5H_4N), 157.9 (2-$C_6H_2{}^tBu_2$ (b)), 152.5 (6-C_5H_4N), 147.6 (d, $^1J_{C-F}$ 248 Hz C_6F_5), 146.1 (5-$C_6H_2{}^tBu_2$ (a or b)), 145.7 (5-$C_6H_2{}^tBu_2$ (a or b)), 144.5 (4-C_5H_4N), 136.6 (d $^1J_{C-F}$ 249 Hz C_6F_5), 135.4 (d $^1J_{C-F}$ 232 Hz C_6F_5), 133.9 (3-$C_6H_2{}^tBu_2$ (a or b)), 133.8 (3-$C_6H_2{}^tBu_2$ (a or b)), 125.8 (5-C_5H_4N), 124.6 (6-$C_6H_2{}^tBu_2$ (a and b)), 124.4 (4-$C_6H_2{}^tBu_2$ (a and b)), 124.0 (3-C_5H_4N), 123.1 (1-$C_6H_2{}^tBu_2$ (a or b)), 122.7 (1-$C_6H_2{}^tBu_2$ (a or b)), 76.9 (Ti-*Me*), 60.5 (N$CH_2C_5H_4N$), 57.0 (NCH_2Ar), 34.4 (3-$C_6H_2(CMe_3)_2$ (a and b)), 34.0 (5-$C_6H_2(CMe_3)_2$ (a and b)), 30.4 (5-$C_6H_2(CMe_3)_2$ (a and b)), 28.7 (3-$C_6H_2(CMe_3)_2$ (a or b), 28.6 (3-$C_6H_2(CMe_3)_2$ (a or b), 8.8 (6H, s, $(C_6F_5)B_3Me$). ^{19}F NMR (dichloromethane-d_2, 282.2 MHz, 183 K): −135.5 (br s, *o*-C_6F_5), −166.6 (br s, *p*-C_6F_5), −169.5 (s, *m*-C_6F_5). IR (NaCl plates, Nujol mull, cm^{-1}): 1783 (vw), 1640 (s), 1614 (s), 1571 (w), 1553 (w), 1510 (vs), 1413 (m), 1366 (s), 1304 (m), 1266 (s), 1238 (s), 1204 (s), 1167 (vs), 1125 (s), 1087 (vs), 1025 (m), 995 (m), 979 (m), 966 (s), 953 (s), 934 (m), 920 (s), 874 (s), 843 (m), 814 (m), 804 (m), 768 (s), 720 (s), 656 (m), 636 (m), 618 (w), 606 (w), 588 (m), 569 (w). Anal. Found (calcd for $C_{112}H_{112}B_2F_{30}N_4O_4Ti_2\cdot 0.3(CH_2Cl_2)$): C, 58.6 (58.9); H, 5.0 (5.0); N, 2.3 (2.4).

NMR Tube Scale Syntheses of $[Ti_2(O_2{}^{tBu}NN')_2Me_2]\cdot 2[B(Ar^F)_4]$ (22-$[B(Ar^F)_4]$). To a yellow solution of $Ti(O_2{}^{tBu}NN')Me_2$ (**14**) (10.0 mg, 0.016 mmol) in dichloromethane-d_2 (0.40 mL) was added a solution of $[Ph_3C][B(Ar^F)_4]$ (14.8 mg, 0.016 mmol) in dichloromethane-d_2 (0.40 mL). The resulting solution turned immediately orange-red and was transferred to a 5 mm J. Young NMR tube. The ^1H NMR spectrum after 5 min showed only resonances attributable to $[\mathbf{22}]^{2+}$and $MeCPh_3$, while the ^{19}F NMR spectrum showed only resonances attributable to $[B(Ar^F)_4]^-$.

NMR Tube Scale Synthesis of $[Ti_2(O_2{}^{Me}NN')_2Me_2]\cdot 2[MeB(Ar^F)_3]$ (23-$[MeB(Ar^F)_3]$). To a yellow solution of $Ti(O_2{}^{Me}NN')Me_2$ (**15**) (8.8 mg, 0.019 mmol) in dichloromethane-d_2 (0.40 mL) was added a solution of $B(Ar^F)_3$ (10.0 mg, 0.019 mmol) in dichloromethane-d_2 (0.40 mL). The resulting solution turned immediately orange-red and was transferred to a 5 mm J. Young NMR tube. The ^1H NMR spectrum after 5 min showed only resonances attributable to $[\mathbf{23}]^{2+}$ and $[MeB(Ar^F)_3]^-$, while the ^{19}F NMR spectrum showed only resonances attributable to $[MeB(Ar^F)_3]^-$.

^1H NMR (dichloromethane-d_2, 500.0 MHz, 293 K): 8.26 (2H, d, ^3J 5.5 Hz 6-C_5H_4N), 7.68 (2H, app. td, app. ^3J 8.0 Hz, ^4J 1.5 Hz, 4-C_5H_4N), 7.15 (2H, at, a ^3J 7.0 Hz, 5-C_5H_4N), 7.07 (2H, s 4-$C_6\mathit{H}_2Me_2$ (a)), 7.02−6.97 (4H, overlapping m, 3-C_5H_4N and 6-$C_6\mathit{H}_2Me_2$ (a)), 6.84 (2H, s, 6-$C_6\mathit{H}_2Me_2$ (b)), 6.75 (2H, s, 4-$C_6\mathit{H}_2Me_2$ (b)), 4.49−4.68 (6H, overlapping m, $NC\mathit{H}_2$), 4.00 (2H, d, ^2J 15.5 Hz, $NC\mathit{H}_2$), 3.68−5.56 (4H, overlapping m, $NC\mathit{H}_2$), 2.34 (12H, overlapping s, 3-$C_6H_2\mathit{Me}_2$ and Ti-*Me*), 2.15 (6H, s, 3-$C_6H_2\mathit{Me}_2$), 2.09 (6H, s, 5-$C_6H_2\mathit{Me}_2$), 1.95 (6H, s, 5-$C_6H_2\mathit{Me}_2$)), 0.50 (6H, s, $(C_6F_5)_3B\mathit{Me}$), The designations (a) and (b) relate resonances to protons on a specific phenoxy group; however which group contains the bridging oxygen could not be determined. ^{19}F NMR (dichloromethane-d_2, 282.2 MHz, 293 K): −133.4 (br s, *o*-C_6F_5), −165.3 (t, ^3J 21.0 Hz, *p*-C_6F_5), −167.9 (app. t, app. ^3J 19.5 Hz, *m*-C_6F_5).

NMR Tube Scale Synthesis of $[Ti_2(O_2{}^{Me}NN')_2Me_2]\cdot 2[B(Ar^F)_4]$ (23-$[B(Ar^F)_4]$). To a yellow solution of $Ti(O_2{}^{Me}NN')Me_2$ (**15**) (10.0 mg, 0.022 mmol) in dichloromethane-d_2 (0.40 mL) was added a solution of $[Ph_3C][B(Ar^F)_4]$ (20.3 mg, 0.022 mmol) in dichloromethane-d_2 (0.40 mL). The resulting solution turned immediately orange-red and was transferred to a 5 mm J. Young NMR tube. The ^1H NMR spectrum after 5 min showed resonances attributable to $[\mathbf{23}]^{2+}$, while the ^{19}F NMR spectrum showed only resonances attributable to $[B(Ar^F)_4]^-$.

Ethylene Polymerization with MAO as Activator: General Procedure. To a sealable metal reactor, containing a glass insert, was added MAO (20 mL, 10% in toluene w/w: 30 mmol, 1500 equiv) in toluene (200 mL). The solution was stirred at 250 rpm for 5 min to remove any water or other impurities. The precatalyst (20 μmol) was dissolved in toluene (50 mL) and added to the reactor, and the mixture was stirred for 30 min at 250 rpm. The reaction vessel was placed under full vacuum for 10 s, the stirring was increased to 750 rpm, and the reactor was placed under a dynamic pressure of 5 bar of dried ethylene (potassium/glass wool). After 1 h, the reactor was vented, and methanol (5 mL) was added to the mixture, followed by water (50 mL). The mixture was acidified to pH 1 using a solution of 10% HCl in methanol. The polymers were filtered, washed with water (1000 mL), and dried to constant weight at room temperature.

Ethylene Polymerization Using $B(Ar^F)_3$, $[Ph_3C][BAr^F{}_4]$, or $[HNMe_2Ph][BAr^F{}_4]$ as Activators: General Procedure. To a sealable metal reactor, containing a glass insert, was added Al^iBu_3 (5 mL, 5 mmol, 250 equiv) in toluene (200 mL). The solution was stirred at 250 rpm for 5 min. The precatalyst (20 μmol) was dissolved in toluene (25 mL) and added to the reactor and stirred for 5 min. The cocatalyst (20 μmol) in toluene (25 mL) was added, and the reactor was placed under full vacuum for 10 s. The stirring was increased to 750 rpm and a dynamic pressure of 5 bar of dried ethylene (potassium/glass wool) applied. After 1 h the polymer was worked up as for the MAO actication experiment (vide supra).

1-Hexene Polymerization with $[Ti_2(O_2{}^{tBu}NN)_2Me_2]\cdot 2[MeB(Ar^F)_3]$ (22-$[MeB(Ar^F)_3]$). To a solution of $Ti(O_2{}^{tBu}NN)Me_2$ (**14**) (12.4 mg, 0.02 mmol) in 1-hexene (20 mL) in a preweighed ampule containing a magnetic stirrer bar was added a solution of $B(Ar^F)_3$ (10.2 mg, 0.02 mmol) in 1-hexene (20 mL). Upon mixing a color change from yellow to orange-red was observed, indicating formation of the species **22**-$MeB(Ar^F)_3$. After 6 h the volatiles were removed under reduced pressure and the sticky residue of polyhexene dried to constant weight under dynamic vacuum. Yield: 0.057 g (after subtraction of mass of catalyst and cocatalyst); activity = 0.50 g $mmol^{-1}\ h^{-1}$. The polyhexene was characterized by comparison with literature ^1H NMR data in $CDCl_3$.[11] Analysis of the polymer by GPC (RAPRA Technology Ltd) gave $M_w = 60\,400$, $M_n = 24\,600$, $M_w/M_n = 2.5$.

Crystal Structure Determinations of $Sc(O_2{}^{tBu}NN')Cl(py)\cdot C_6H_6$ ($\mathbf{2}\cdot C_6H_6$), $Sc_2(O_2{}^{Me}NN')_2Cl_2\cdot 2CH_2Cl_2$ ($\mathbf{3}\cdot 2CH_2Cl_2$), $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2\cdot 3(C_6H_6)$ ($\mathbf{4}\cdot 3C_6H_6$), $Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (11), $Ti(O_2{}^{tBu}NN')Cl_2\cdot CH_2Cl_2$ ($\mathbf{9}\cdot 0.5CH_2Cl_2$), $Ti(O_2{}^{Me}NN')Cl_2\cdot 2.5C_6H_6$ ($\mathbf{10}\cdot 2.5C_6H_6$), $Ti(O_2{}^{tBu}NN')(N^tBu)(py)\cdot 2C_6H_6$ ($\mathbf{16}\cdot 2C_6H_6$), $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2\cdot 3CH_2Cl_2$ ($\mathbf{18}\cdot 3CH_2Cl_2$), $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)\cdot 0.5C_6H_6$ ($\mathbf{20}\cdot 0.5C_6H_6$), and $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(py)$ (21). Crystal data collection and processing parameters are given in Table 11. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. Intensity data were processed using the DENZO-SMN package.[43] The structures were solved using the direct-methods program SIR92,[44] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[45] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. Weighting schemes were applied as appropriate. Full listings of atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Center. See Guidelines for Authors, Issue No. 1.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $Sc(O_2{}^{tBu}NN')Cl(py)\cdot C_6H_6$ ($\mathbf{2}\cdot C_6H_6$), $Sc_2(O_2{}^{Me}NN')_2Cl_2\cdot 2CH_2Cl_2$ ($\mathbf{3}\cdot 2CH_2Cl_2$), $Y_2(O_2{}^{tBu}NN')_2(\mu\text{-}Cl)_2(py)_2\cdot 3(C_6H_6)$ ($\mathbf{4}\cdot 3C_6H_6$), $Ti(O_2{}^{tBu}NN')(NMe_2)_2$ (**11**), $Ti(O_2{}^{tBu}NN')Cl_2\cdot CH_2Cl_2$ ($\mathbf{9}\cdot 0.5CH_2Cl_2$), $Ti(O_2{}^{Me}NN')Cl_2\cdot 2.5C_6H_6$ ($\mathbf{10}\cdot 2.5C_6H_6$), $Ti(O_2{}^{tBu}NN')(N^tBu)(py)\cdot 2C_6H_6$ ($\mathbf{16}\cdot 2C_6H_6$), $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2\cdot 3CH_2Cl_2$ ($\mathbf{18}\cdot 3CH_2Cl_2$), $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3Me_2)(py)\cdot 0.5C_6H_6$ ($\mathbf{20}\cdot 0.5C_6H_6$), and $Ti(O_2{}^{tBu}N)(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(py)$ (**21**).This material is available free of charge via the Internet at http://pubs.acs.org.

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