New Bulky Bis(amino)cyclodiphosph(III)azanes and Their Titanium(IV) Complexes: Synthesis, Structures and Ethene Polymerization Studies

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Bis(amino)cyclodiphosph(III)azanes *cis*-[(RNH)(PN-*t*Bu)]$_2$, R = 2,6-*i*Pr$_2$C$_6$H$_3$ (**2**), 2-*t*BuC$_6$H$_4$ (**3**), 2-CF$_3$C$_6$H$_4$ (**4**), 2,5-*t*Bu$_2$C$_6$H$_3$ (**5**), Ph$_2$CH (**6**), 2,4-Me$_2$C$_6$H$_3$ (**7**), 2,6-Et$_2$C$_6$H$_3$ (**8**), have been synthesized in the presence of Et$_3$N by a nucleophilic substitution reaction of *cis*-(ClPN-*t*Bu)$_2$ (**1**) with the corresponding bulky aryl and alkylamines. The bis(amino)-cyclodiphosph(III)azanes **2**–**8** adopt the thermodynamically stable *cis*-configuration – a prerequisite for efficient metal complex formation. Deprotonation of bis(amino)cyclodiphosph(III)azanes with *n*BuLi slowly afforded the corresponding salts, *cis*-[(2,4-Me$_2$C$_6$H$_3$N)(PN-*t*Bu)]$_2$Li$_2$(THF)$_2$. The crystal structure of *cis*-[(2,4-Me$_2$C$_6$H$_3$N)(PN-*t*Bu)]$_2$Li$_2$(THF)$_2$ (**9**) consists of a heterocube of two lithium atoms, two nitrogen atoms and a cyclodiphosph(III)azane ring. Transmetallation of Li compounds by TiCl$_4$ was unselective and led to a complex mixture of products. The direct reaction of *cis*-bis(amino)cyclodiphosph(III)azanes with Ti(NMe$_2$)$_4$ is the most efficient method to prepare the corresponding titanium(IV) bis-amido complexes *cis*-[(RN)(PN*t*Bu)]$_2$Ti(NMe$_2$)$_2$ (**11a**, **12a**, **14a**, **15a**). In the solid state, *cis*-[(PhN)(PN-*t*Bu)]$_2$Ti(NMe$_2$)$_2$ (**11a**) adopts a highly distorted trigonal-bipyramidal configuration at the metal center. These bis-amido titanium(IV) complexes have been subsequently transformed into the dichlorides *cis*-[(RN)(PN-*t*Bu)]$_2$TiCl$_2$ (**12**–**15**) with Me$_3$SiCl. After MAO activation the complexes possess moderate catalytic activity in ethene polymerization and produce linear polyethylene with molar masses of up to 2.6×10^6 g/mol and with narrow polydispersities. The catalytic activity and polymer properties depend strongly on the bulkiness of the ligand substituents; *cis*-[(2,6-*i*Pr$_2$C$_6$H$_3$N)(PN-*t*Bu)]$_2$TiCl$_2$ (**14**) gave the highest activity (231 kg PE/mol$_{cat}$ × bar × h).

Introduction

The highly efficient homogeneous α-olefin polymerization catalysts based on methylalumoxane (MAO) activated Group 4 metallocene dichlorides have stimulated intensive polymerization catalysis research over the past three decades.[1] The major focus has been on the preparation of various *ansa*-metallocenes, especially ones intended for the stereoselective polymerization of propene.[2] Numerous studies have also been made on late transition metal complexes,[3] constrained geometry catalysts[4] and complexes of Group 4 metals with non-cyclopentadienyl ligands. The substantial progress on non-metallocene polymerization catalysis has been achieved by both the "right" choice of a transition metal and the rational design of the ligand systems. Recent highly successful catalysts have been based on titanium and zirconium phenoxyimino-type complexes having novel polymerization properties,[5] as well as on highly efficient C_1-symmetric Group 4 pyridyl-amine catalysts aimed for isospecific propene polymerization.[6]

Ligands containing heteroatoms (e.g. phosphorus, nitrogen) are candidates for catalyst components because they bind strongly to the early transition metals and their mode of coordination as well as ligand hapticity can be varied.[7a] This allows the electronic character, geometric properties and steric protection of the catalytic center to be modified.[7] Bis(amido) complexes of titanium(IV) have attracted considerable attention because of their high activity in ethene polymerization after activation with MAO.[7,8] Thus, we found bis-amino type *cis*-2,4-bis(amino)cyclodiphosph(III)-azanes of the general formula *cis*-[(RNH)(PN-*t*Bu)]$_2$ to be interesting ligand precursors for olefin polymerization catalysts. The coordination chemistry of simple *cis*-2,4-bis(amino)cyclodiphosph(III)azanes, namely *cis*-[(*t*BuNH)(PN-*t*Bu)]$_2$ and *cis*-[(PhNH)(PN-*t*Bu)]$_2$ (structure A), has been described in the synthesis of both main group compounds[9] and titanium(IV), zirconium(IV) and hafnium(IV) complexes (structure B).[10,11,12] Their polymerization properties have not, to our knowledge, been published.

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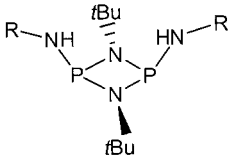
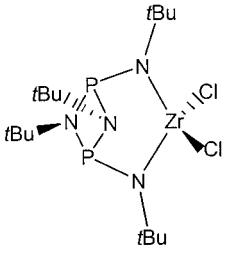


R = *t*Bu, Ph

A



M - Ti, Zr, Hf

B

The relatively straightforward synthesis of various *cis*-2,4-bis(amino)cyclodiphosph(III)azanes make them attractive candidates to study the ligand's influence on the polymerization properties. In the present work, a synthetic approach to new *cis*-2,4-bis(amino)cyclodiphosph(III)azane ligands, *cis*-[(RNH)(PN-*t*Bu)]$_2$ (**2**–**8**), bearing bulky amino substituents and their titanium(IV) complexes has been developed and ethene polymerization studies carried out.

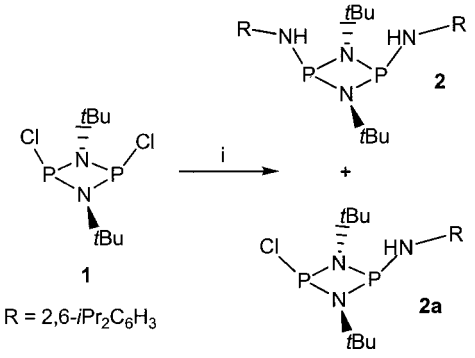
Results and Discussion

Ligand Synthesis

Phosphazanes, both cyclic and acyclic,[13] are stable P–N compounds that are easily synthesized. Cyclodiphosph(III)-azanes (containing a P_2N_2 moiety) were first reported by Michaelis and Schroeter in 1894[14] but were fully characterized only in the 1970s.[15,16] They have attracted most attention as precursors for hybrid (organic-inorganic) P–N polymeric materials,[16c] and as ligand precursors for the synthesis of main group element compounds[9] and some, still rare, early transition metal complexes.[10,11,12] They preparation, in good yield, is commonly based on the reaction of *cis*-(ClPN-*t*Bu)$_2$ (**1**) with either lithium amide or an excess of a free amine.[9] We investigated both of these methods to access the new, bulky bis(amino)cyclodiphosph(III)azanes.

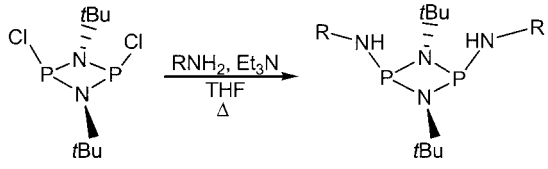
However, some modifications of these general procedures became necessary as, for instance, 2,4-dimethylphenyllithiumamide in THF reacted with **1** nonselectively, and according to ^{31}P NMR data the cyclodiphosph(III)azane P_2N_2 ring was destroyed. Direct aminolysis of the P–Cl bond with free amines was then explored but, even under severe conditions, direct substitution was negligible. For example, **1** and 2,6-diisopropylphenylamine, failed to react under various conditions, even after refluxing in THF for one week; ^{31}P NMR data revealed only the starting compound **1** and the free amine. Apparently, the nucleophilic substitution did not take place because of the steric demand of the amine.

Another synthetic possibility is the application of Et_3N as a base in the reaction of **1** with bulky arylamines.[9] Thus, the reaction of **1** with 2,6-diisopropylphenylamine and an excess of Et_3N (4 equiv.), after refluxing for four days, gave, finally, the desired disubstituted compound *cis*-[(2,6-*i*Pr$_2$C$_6$H$_3$NH)(PN-*t*Bu)]$_2$ (**2**) in good yield. Further experiments with different ratios of reactants and reaction times showed the limitations of this reaction; the selectivity depends strongly on the ratio of arylamine to Et_3N, and on the refluxing time (Scheme 1). This optimized synthetic procedure was then applied to give various bis(amino)cyclodiphosph(III)azanes (**3**–**8** in Scheme 2).



i - 2 equiv. RNH_2, 2 equiv. Et_3N in THF, 4 days refluxing (40% **2**, 60% **2a**)
or 2 equiv. RNH_2, 4 equiv. Et_3N in THF, 2 days refluxing (70% **2**, 30% **2a**)
or 2 equiv. RNH_2, 2 equiv. Et_3N in THF, 4 days refluxing (100% **2**, 0% **2a**)

Scheme 1



2, R = 2,6-*i*Pr$_2$C$_6$H$_3$
3, 2-*t*BuC$_6$H$_4$
4, 2-CF$_3$C$_6$H$_4$
5, 2,5-*t*Bu$_2$C$_6$H$_3$
6, Ph$_2$CH
7, 2,4-Me$_2$C$_6$H$_3$
8, 2,6-Et$_2$C$_6$H$_3$

Scheme 2

Et_3N acts as more than a simple Brönsted base that scavenges the generated HCl – at least four equivalents of it are required to obtain good yields. Some of the Et_3N can assist the nucleophilic substitution by coordination and polarization of the P–Cl bonds of (ClPN-*t*Bu)$_2$ (**1**), while the rest acts as a traditional Brönsted base.

Structure of the Bis(amino)cyclodiphosph(III)azanes

The obtained bis(amino)cyclodiphosph(III)azanes are colorless, air-sensitive oils or solids that are very soluble even in aliphatic hydrocarbon solvents. Despite the long refluxing times, the reactions proceed selectively and, according to ^{31}P NMR, yield only one product from each reaction. Bis(amino)cyclodiphosph(III)azanes can exist as *cis* and

trans isomers; the differences in chemical shifts in the ^{31}P NMR spectra indicate which is present.[17] According to NMR spectroscopic data, the synthesized bis(amino)cyclodiphosph(III)azanes (**2**–**8**) adopt the synthetically more desirable, and thermodynamically more stable, *cis*-conformation (Exp. Sect.).

The single-crystal X-ray measurements of **3**–**5** also support the exclusive presence of the *cis*-isomer. The solid-state structures (Figures 1–3) and selected structural parameters (Table 1) are presented here. The solid-state structures reveal that the P_2N_2 cyclodiphosph(III)azane rings are bent from the mean plane. Such disturbance of the P_2N_2 rings accords with the results of earlier molecular orbital calculations for *cis*-cyclodiphosph(III)azanes with small amino substituents,[18] and may be caused by repulsive lone pair–bond pair electronic interactions.[9] Despite the sterically bulky aryl or alkyl substituents on these bis(amino)cyclodiphosph(III)azanes the basic structural features (bond lengths and angles) of the ligand backbone are rather similar to ones reported earlier (Table 1).

The solid-state structure of *cis*-[(2-*t*BuC_6H_4NH)(PN-*t*Bu)]$_2$ (**3**) (Figure 1), which has only monosubstituted aniline groups, resembles that established for *cis*-[(PhNH)(PN-*t*Bu)]$_2$.[9,12] In both structures, the *tert*-butyl groups on the P–N ring are bent towards the P_2N_2 mean plane [for **3**: C(1)–P_2N_2 plane 161.05(3)° and C(5)–P_2N_2 plane 170.94(3)°] and the orientation of the anilines gives an overall C_{2v} symmetry. The slight asymmetry of the P_2N_2 ring in **3** is reflected by the P–N endocyclic bond lengths, which vary from 1.707(3) to 1.728(3) Å.

The structural features of *cis*-[(2-$CF_3C_6H_4$NH)(PN-*t*Bu)]$_2$ (**4**) resemble those of **3** (Figure 2). The electron-with-

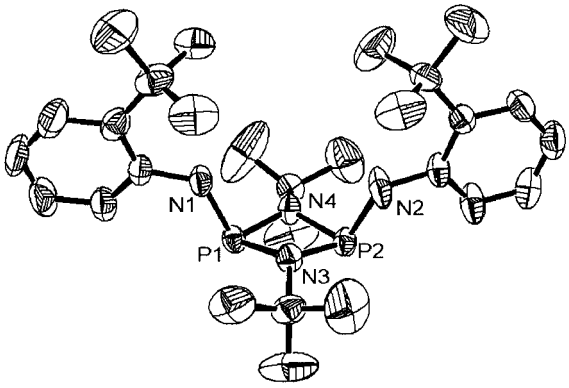


Figure 1. ORTEP diagram of *cis*-[(2-*t*BuC_6H_4NH)(PN-*t*Bu)]$_2$ (**3**)

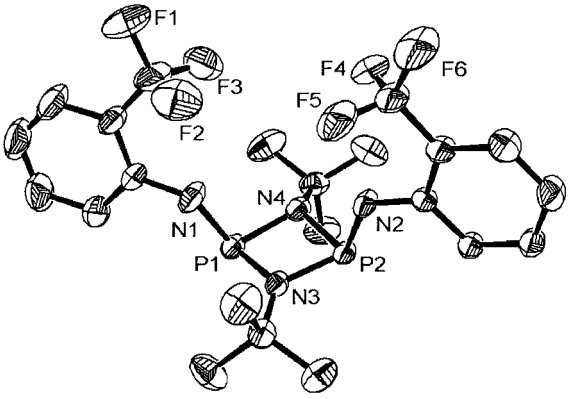


Figure 2. ORTEP diagram of *cis*-[(2-$CF_3C_6H_4$NH)(PN-*t*Bu)]$_2$ (**4**)

Table 1. Selected structural parameters for ligands **3**–**5**

	3	**4**	**5**	*cis*-[(*t*BuNH)(*t*BuNP)]$_2$ [20]	*cis*-[(PhNH)(*t*BuNP)]$_2$ [9]
Distances, Å					
P1–N3	1.728(3)	1.7063(15)	1.705(3)	1.721(2)	
P1–N4	1.707(3)	1.7256(17)	1.734(3)	1.730(2)	
P2–N3	1.726(3)	1.7072(16)	1.716(3)	1.730(2)	1.726(2)
P2–N4	1.715(3)	1.7184(16)	1.724(3)	1.721(2)	
P1–P2	2.5910(13)	2.5937(7)	2.5997(1)	2.600(2)	2.583(1)
P2–N2	1.680(3)	1.7064(15)	1.695(2)	1.664(2)	1.689(2)
N3–C1	1.485(5)	1.472(3)	1.473(4)	1.485(3)	
N4–C5	1.474(4)	1.481(3)	1.485(4)	1.485(3)	
N1–C9	1.403(4)	1.400(3)	1.411(4)	1.470(3)	
Angles, deg					
N3–P1–N4	80.56(14)	81.08(8)	80.67(13)	80.88(1)	
P1–N3–P2	97.20(15)	98.90(9)	98.92(14)	97.83(1)	
P1–N4–P2	98.43(15)	97.72(8)	97.50(14)	97.83(1)	
C1–N3–P1	125.5(2)	130.96(13)	129.8(2)	124.8(2)	
C5–N4–P1	128.5(2)	124.79(13)	124.9(2)	125.1(2)	
N2–P2–N4	105.01(18)	101.80(8)	101.60(13)	104.69(1)	
N2–P2–N3	101.15(16)	105.20(8)	106.21(13)	105.03(1)	
C9–N1–P1	128.1(3)	127.01(16)	125.8(2)	130.2(2)	
C23–N2–P2			127.3(2)		
C22–N2–P2					

drawing CF_3 substituents on the aniline groups have a significant influence only on the P(2)−N(2) and P(1)−N(1) bond lengths, while the puckering of the P_2N_2 ring is fairly similar to that for **3**. Owing to the second *tert*-butyl group on the aniline moiety *cis*-[(2,5-di-*t*BuC_6H_3NH)(PN-*t*Bu)]$_2$ (**5**) (Figure 3) has lost its superfacial C_{2v} symmetry. The bond lengths and angles in the P_2N_2 ring are nevertheless similar to those of **3**.

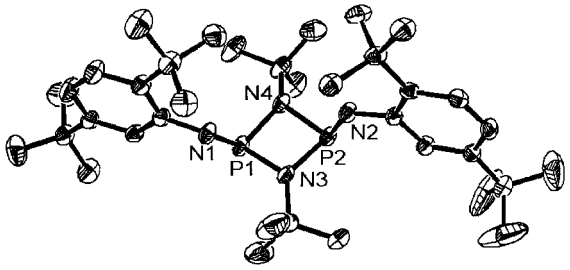
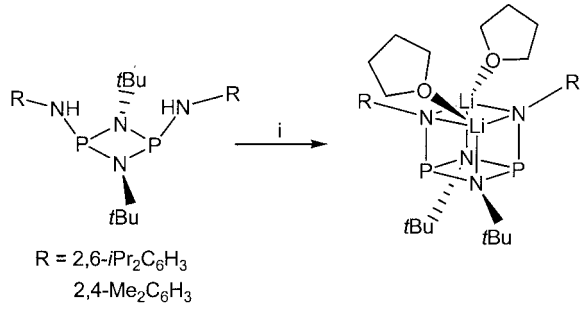


Figure 3. ORTEP diagram of *cis*-[(2,5-tBu$_2C_6H_3$NH)(PN-*t*Bu)]$_2$ (**5**)

Synthesis of Titanium(IV) Complexes

Of the various literature methods for the preparation of early transition metal complexes the general route is the transmetallation reaction between transition metal halides and alkali or alkaline earth metal salts of the ligand.[19] Applying a procedure described earlier,[20] the desired dilithium salts of *cis*-[(2,6-di-*i*PrC_6H_3NH)(PN-*t*Bu)]$_2$ (**2**) (see supporting information) and *cis*-[(2,4-di-MeC_6H_3NH)(PN-*t*Bu)]$_2$ (**7**) were prepared in THF (Scheme 3). According to the ^{1}H and ^{13}C NMR spectra, the lithium salts contains two coordinated THF molecules. The phosphorus signal at 163.01 ppm in the ^{31}P NMR spectrum confirms the formation of the lithium salt *cis*-[(2,4-di-MeC_6H_3N)(PN-*t*Bu)]$_2$-Li$_2$(THF)$_2$ (**9**).[21]



i - *n*BuLi, THF, reflux, 5h

Scheme 3

Recrystallization of the dilithium salt **9** from THF/hexane solution provided crystals suitable for X-ray study (Figure 4). Selected bond lengths and angles are collected in Table 2. The P_2N_2 ring is almost planar, which is also related to the symmetry of the molecule and to the equal bond lengths in the ring. The P_2N_2 ring, exocyclic N, and both Li atoms form an inorganic heterocube that is surrounded by the aniline groups of the ligand and two coordinated THF molecules. The exocyclic P−N bonds are shorter than the endocyclic ones [1.674(3) vs. 1.768(3) Å]. The bond lengths between Li and the exocyclic nitrogen atoms are almost equal [from 2.071(6)Å to 2.095(6)Å] and similar to those in related lithium amides [Li−N in {Li[N(SiMe$_3$)$_2$]OEt$_2$}$_2$ are 2.06(1) Å].[22] Thus, the solid-state structure of compound **9** has similar features to those described for *cis*-[(*t*BuN)(PN-*t*Bu)]$_2$Li$_2$(THF)$_2$,[21] but in **9** the lithium atom and endocyclic nitrogen atoms are further apart [2.133(6) Å] and can be considered typical for bonds between a coordinated lithium cation and a donor nitrogen atom.

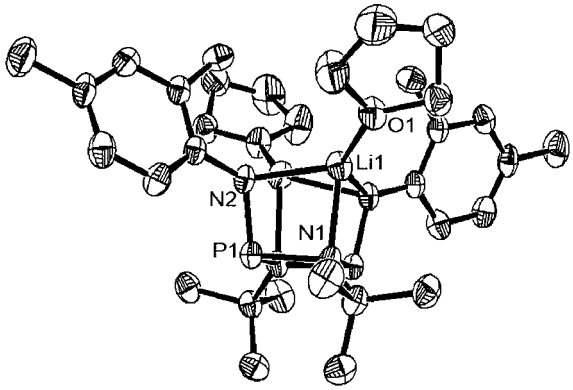


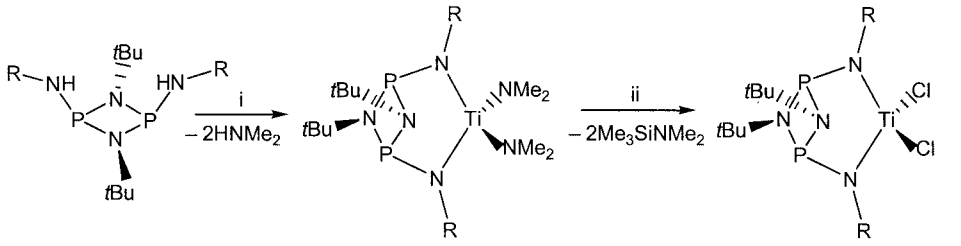
Figure 4. ORTEP diagram of *cis*-[(2,4-Me$_2C_6H_3$N)(PN-*t*Bu)]$_2$Li$_2$-(THF)$_2$ (**9**); one solvent molecule is omitted for clarity

Table 2. Selected structural parameters for compound **9**

Distances, Å			
P1−N1	1.768(3)	N2−Li1	2.133(6)
P1−N1a[a]	1.752(3)	N2−Li1a	2.095(6)
P1−N2	1.674(3)	Li1−Li1a	2.612(1)
P1−P1a	2.635(2)	Li1−O1	1.911(6)
N1−C1	1.492(4)	N2−C5	1.408(4)
N1−Li1	2.071(6)		
Angles, deg			
N1−P1−N1a	83.06(1)	N2−Li1−N2a	99.70(2)
P1−N1−P1a	96.92(1)	N1−Li1−N2	76.90(2)
N2−P1−N1	98.83(1)	Li1−N1−C1	123.80(2)
N2−P1−N1a	98.29(1)	C1−N1−P1	122.10(2)
Li1−N1−P1	91.76(2)	N1−Li1−O1	123.60(3)
Li1−N1−P1a	91.55(2)	O1−Li1−N2	121.80(3)
Li1−N2−Li1a	76.30(2)	C5−N2−Li1	127.10(2)
Li1−N2−P1	92.31(2)	C5−N2−Li1a	136.0(3)

[a] Label "a" means a symmetry equivalent atom at $-x$, y, $-z + 1/2$.

To synthesize titanium(IV) dichloride complexes from the *cis*-2,4-bis(amino)cyclodiphosph(III)azanes the above-described lithium salts were treated with $TiCl_4$. Surprisingly, the transmetallation reaction failed and led to a complex mixture of unidentified products. Only one complex, [(*t*BuN)$_2$(PN-*t*Bu)$_2$]$TiCl_2$ (**10**), previously synthesized by Stahl et al.[23] was obtained. This might be due either to the



11, R = Ph
12a, Ph_2CH
13a, 2,6-$Et_2C_6H_3$
14a, 2,6-$iPr_2C_6H_3$
15a, 2,5-$tBu_2C_6H_3$

12, R = Ph_2CH
13, 2,6-$Et_2C_6H_3$
14, 2,6-$iPr_2C_6H_3$
15, 2,5-$tBu_2C_6H_3$

i - $Ti(NMe_2)_4$, toluene, reflux; ii - excess of Me_3SiCl

Scheme 4

steric demand of the obtained lithium {see the solid-state structure of [(2,4-di-MeC_6H_3N)(*t*BuNP)]$_2Li_2(THF)_2$ (**9**)} salts, which slow down the reaction, or to titanium tetrachloride, a strong Lewis acid, which may attack the P−N bond of the P_2N_2 cycle or the phosphorus lone pair more readily than a N−Li or N−Mg bond.

An alternative approach, the direct metallation of the ligand precursors through amine elimination,[24] turned out to be efficient. The reaction of the less Lewis-acidic $Ti(NMe_2)_4$ with [(RNH)(*t*BuNP)]$_2$ (**2**, **5**, **6**, **8**) occurred selectively, according to ^1H and ^{31}P NMR data, and the bis-amido complexes [(RNH)(*t*BuNP)]$_2Ti(NMe_2)_2$ (**11a**−**15a**) were formed (Scheme 4). Such bis-amido complexes are usually oils, and are highly soluble in aliphatic solvents, making their separation and purification difficult. Therefore, they were characterized on the basis of ^1H, ^{13}C and ^{31}P NMR spectroscopic data (see Supporting Information). Their ^1H NMR spectra revealed the C_{2v} symmetry expected for such titanium(IV) complexes and indicate the equivalence of all alkyl and aromatic substituents. Only the ligand precursor **4**, with electron-withdrawing CF_3 substituents, behaved differently, and complex formation under similar reaction conditions was incomplete.

With *cis*-[$(PhN)_2$(PN-*t*Bu)$_2$]$Ti(NMe_2)_2$ (**11a**), crystals suitable for X-ray analysis were obtained from a saturated hexane solution at −20 °C. The ORTEP diagram of **11a** (Figure 5) and selected bond lengths and angles (Table 3) are given here. In the solid state, four metal−amide bonds and an additional donor bond from one of the cyclophosph(III)azane ring nitrogen atoms define a highly distorted trigonal-bipyramidal coordination at the central titanium atom, reducing the symmetry of this molecule from C_2 to C_s in the solid state. In general, the coordination sphere of **11a** resembles previously described structures for Ti, Zr and Hf complexes based on the *cis*-[(*t*BuNH)(PN-*t*Bu)]$_2$ ligand.[10,11,12] The cyclophosph(III)azane ring is almost planar and the phenyl rings are almost perpendicular to the P_2N_2 plane and, hence, leave the metal center relatively open to nucleophilic attack.

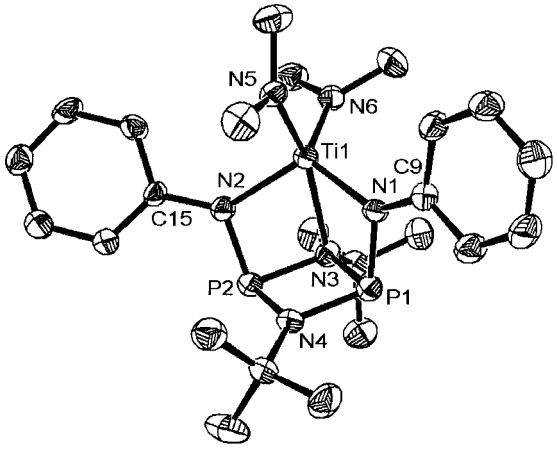


Figure 5. ORTEP diagram of *cis*-[(PhN)(PN-*t*Bu)]$_2Ti(NMe_2)_2$ (**11a**)

Table 3. Selected structural parameters for compound **11a**

Distances, Å			
Ti−N3	2.325(4)	P1−N3	1.791(4)
Ti−N1	2.020 (3)	P2−N3	1.770(4)
Ti−N2	2.011(3)	P1−N4	1.731(4)
Ti−N5	1.907(4)	P2−N4	1.728(4)
Ti−N6	1.884(4)	P1−P2	2.653(2)
P1−N1	1.708(4)		
Angles, deg			
N5−Ti−N6	98.66(2)	N5−Ti−N3	159.82(2)
N1−Ti−N2	111.80(1)	N6−Ti−N3	101.39(2)
N1−Ti−N5	101.26(2)	N1−P1−P2	101.73(1)
N1−Ti−N6	121.14(2)	N3−P1−N4	81.38(2)
N5−Ti−N2	98.67(2)	P1−N3−P2	96.32(2)
N6−Ti−N2	118.99(2)	P1−N4−P2	100.15(2)

The additional nitrogen is rather weakly coordinated, as indicated by the elongated bond length [2.325 (4) Å], which is significantly longer than the 2.267 (2) Å in the related

compound $[(t\text{BuN})_2(\text{PN-}t\text{Bu})_2]\text{TiCl}_2$).[11] This may be due to NMe_2 substituents donating additional electron density from the sp^2-hybridized amido nitrogen atoms to the metal center, thereby decreasing the Lewis acidity of the titanium. Four amido nitrogen atoms are in a pseudo-tetrahedral environment around the metal center [N(1)−Ti−N(2) and N(5)−Ti−N(6) are 111.80 (1)° and 98.66 (2)° respectively] and the amido N−Ti bond lengths vary from 1.884 (4) to 2.020 (3) Å (Table 3).

Dichlorotitanium(IV) complexes are preferred as catalyst precursors in olefin polymerization due to their higher activity than the corresponding bis(amido) derivatives.[1a] The standard transformation of early transition metal bis(amido) complexes into their dichloride derivatives involves the reaction with an excess of Me_3SiCl.[25] Thus, we treated $[(RN)_2(\text{PN-}t\text{Bu})_2]\text{Ti}(NMe_2)_2$ (**11a**, **12a**, **14a**, **15a**) with an excess of Me_3SiCl (Scheme 4). The one-pot synthesis of $[(RN)_2(\text{PN-}t\text{Bu})_2]\text{TiCl}_2$ complexes is also possible, starting from a ligand precursor, tetrakis(dimethylamido)-titanium(IV) and Me_3SiCl (see Exp. Sect., **13**).

Evaporation of all solvents, followed by extraction with a mixture of CH_2Cl_2/hexane, gave the dichloro titanium(IV) complexes $[(RN)_2(\text{PN-}t\text{Bu})_2]\text{TiCl}_2$ (**12−15**) in good yield. All ^{1}H NMR spectra display a clear singlet at δ = 1.0−1.4 ppm for the imido *t*Bu groups, peaks at δ = 1.0-4.0 ppm for the alkyl substituents, and signals at δ = 7.0−7.8 ppm for the aromatic protons (see supporting information). Phosphorus signals in the ^{31}P NMR spectra appear in the same region as the peaks of the corresponding ligand. This indicates the covalent character of the Ti−amido bond, whereas in the lithium salts the Li−N bonds are strongly polarized.

With *cis*-$[(\text{PhN})_2(\text{PN-}t\text{Bu})_2]\text{Ti}(NMe_2)_2$ (**11a**), amine elimination by Me_3SiCl was unselective and led to the destruction of the parent bis-amido complex. This can be taken as a limitation of the synthetic route, since, without sufficient steric hindrance from the ligand side, breakage of the Ti−N phosphazane amido bond may occur instead of breakage of the Ti−N dimethylamido bond. Apparently, the phenyl group alone is not bulky enough to sufficiently protect the bonding between the metal center and ligand moiety and may be a reason for the lack of selectivity.

Ethene Polymerization

In addition to the preparative chemistry described above the ligand's influence on the titanium(IV) complexes in ethene polymerization was also investigated. After methylalumoxane (MAO) activation all dichloro titanium(IV) complexes $[(RN)_2(\text{PN-}t\text{Bu})_2]\text{TiCl}_2$ (**12−15**), regardless of polymerization temperature, produced high molar mass linear polyethylene. The polymerization results and the properties of the obtained polymers are summarized in Table 4.

Catalyst **10**/MAO bearing *tert*-butyl groups showed a remarkably high initial catalytic activity that severely declined after a few minutes (Figure 6, curve a). The polyethene produced had a high molar mass and a bimodal molar mass distribution, indicating at least two different active centers (run 1 in Table 4; M_w1 = 1 927 000 g/mol, M_w2 = 42 000 g/mol, for GPC curve see supporting information). After activation with MAO, complexes **12** with diphenylmethylamino substituents gave lower initial activities than **10**/MAO, but the steady state consumption of ethene was higher (run 2 in Table 4, curve b in Figure 6). Catalyst precursors **13** and **15** are slowly activated by MAO (Figure 6, curves c and e, respectively) but the high steady state of **15**/MAO is noteworthy. The polymers obtained with **12**/MAO and **13**/MAO exhibit a low molar mass shoulder in the GPC curve, which also explains the relatively large polydispersity (PD) values. **15**/MAO produces ultrahigh molar mass polyethene (M_w = 2.56 × 10^6 g/mol, M_w/M_n = 2.8).

Complex **14**/MAO displayed a combination of high initial activity and slow decline in productivity (Figure 6, d). After one hour of polymerization with the catalysts under similar conditions, the highest polymerization activity was recorded for **14**/MAO (121 kg of PE/(mol_{cat} × bar × h) (run 5 in Table 4). The polymer also exhibited a high molar mass (2.6 × 10^6 g/mol) and a narrow PD (2.17). In a further study, we examined the influence of catalyst concentration and polymerization temperature. Lower amounts of catalyst resulted in higher activities with no significant change in the molar mass of the polymers. For example, when the amount of catalyst **14**/MAO was halved (from 20 μmol to 10 μmol) and then to 5 μmol, the polymerization activity increased from 121 to 143 and 231 kg of PE/(mol_{cat} × bar

Table 4. Data for ethylene polymerization

Entry no.[a]	Catalyst	Concentration (μmol)	Reaction temp. (°C)	Time (min)	Yield (g)	Activity[b]	M_w (g/mol)	M_w/M_n	T_m (°C)
1	**10**	20	50	30	4.22	111	818 000	14.17	135.3
2	**12**	20	50	20	2.1	79	1 897 000	4.70	139.0
3	**13**	10	50	60	3.33	87.6	1 479 000	5.18	139.0
4	**14**	10	50	60	5.45	143.4	2 465 000	4.17	140.7
5	**14**	20	50	60	9.23	121	2 558 000	2.17	140.3
6	**14**	10	70	60	6.24	164.2	1 369 000	2.19	137.7
7	**14**	5	50	30	2.2	231.6	2 375 000	4.32	141.7
8	**15**	10	50	30	2.1	110.5	2 008 000	2.73	139.7
9	**15**	10	70	60	1.74	45.8	2 564 000	2.84	140.7
10	**15**	20	50	60	4.38	57.9	2 268 000	3.70	141.0

[a] MAO (Al/M = 1000), toluene (200 mL), ethylene (3.8 bar). [b] kg PE/(mol_{cat} × bar × h).

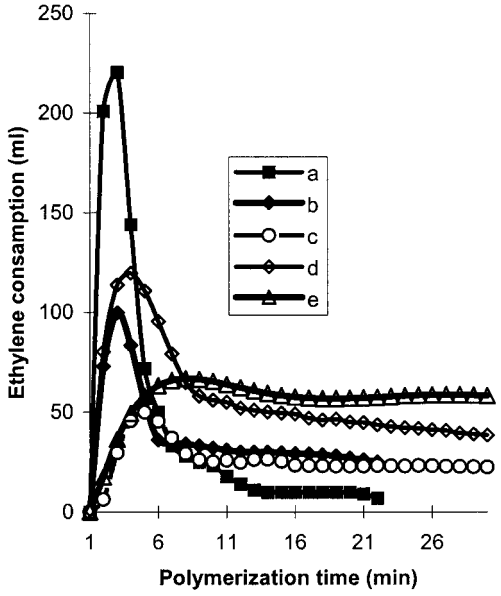


Figure 6. Ethylene consumption curves from polymerization experiments with (a) $[(t\text{BuN})(t\text{BuNP})]_2TiCl_2$ (**10**), (b) $[(Ph_2CHN)(t\text{BuNP})]_2TiCl_2$ (**12**), (c) $[(2,6\text{-}Et_2PhN)(t\text{BuNP})]_2TiCl_2$ (**13**), (d) $[(2,6\text{-}i\text{Pr}_2PhN)(t\text{BuNP})]_2TiCl_2$ (**14**), and (e) $[(2,5\text{-}t\text{Bu}_2PhN)(t\text{BuNP})]_2TiCl_2$ (**15**) as catalyst precursors

$\times$ h) (runs 5, 4 and 7, respectively, in Table 4). This indicates that mass transfer effects play an important role. On increasing the temperature from 50 to 70 °C (runs 5 and 6), the molar mass of the polymers clearly decreases, from 2.5 to 1.4 $\times$ 10^6 g/mol, while the PD is the same. This reveals that catalyst **14**/MAO is stable at higher temperatures.

From the results above, it appears that the catalytic performance of the bis(amido)cyclodiphosph(III)azane titanium(IV)dichlorides depends strongly on the ligand substituents. Activation with MAO was faster for the amido complexes $[(t\text{BuN})(t\text{BuNP})]_2TiCl_2$ (**10**) and $[(Ph_2CHN)(t\text{BuNP})]_2TiCl_2$ (**12**) than for the complexes **13**−**15** with aniline substituents. Moreover, the rate of decline of the polymerization and the steady state values depend on the catalyst precursors used. This indicates that the steric bulkiness of the ligand substituents can influence a sensitive equilibrium between active and dormant metal centers. The bulkiest aniline complex, **15**/MAO, exhibited the highest steady state activities followed by *cis*-$[(2,6\text{-}i\text{Pr}_2C_6H_3N)_2(PN\text{-}t\text{Bu})_2]TiCl_2$ (**14**) and *cis*-$[(2,6\text{-}Et_2C_6H_3N)_2(PN\text{-}t\text{Bu})_2]TiCl_2$ (**13**), i.e. in the order of steric bulkiness.

The polymerization behavior of **10**/MAO ($[(t\text{BuN})(t\text{BuNP})]_2TiCl_2$) is unique due to the bimodal molar mass distribution of the polymer. The relatively small *tert*-butyl groups not only leave the titanium center open for activation and polymerization but, at the same time, the catalyst is susceptible to side reactions. Coordination of the Lewis acidic cocatalyst (MAO) to the lone-pair electrons of phosphorus atoms can initiate destruction of the ligand,[11] which could explain the presence of different active centers and could also be one reason for the fast catalyst deactivation. Therefore, bulky aromatic groups attached directly to the amido nitrogen (**13**−**15**) have two roles: they protect the catalytic active center from side reactions and they prevent the phosphorus atoms of the ligand from destructive coordination to MAO.

Conclusion

New bis(amino)cyclodiphosph(III)azanes *cis*-$[(RNH)(PN\text{-}t\text{Bu})]_2$ **2**−**8** [R = 2,6-$i\text{Pr}_2C_6H_3$ (**2**), 2-$t\text{BuC}_6H_4$ (**3**), 2-$CF_3C_6H_4$ (**4**), 2,5-$t\text{Bu}_2C_6H_3$ (**5**), Ph_2CH (**6**), 2,4-$Me_2C_6H_3$ (**7**), 2,6-$Et_2C_6H_3$ (**8**)] bearing bulky substituents have been synthesized. According to NMR spectroscopic data and single-crystal X-ray analysis, all compounds adopt the thermodynamically more stable *cis*-configuration. Bis(amino)cyclodiphosph(III)azanes can be deprotonated with *n*BuLi, but an extended reaction time is required for complete formation of the lithium salts. The straightforward method of $TiCl_4$ transmetallation of these Li salts proceeded unselectively and gave a complex mixture of products. Direct reaction of $[(RNH)(t\text{BuNP})]_2$ (**2**, **5**, **6**, **8**) with the less Lewis acidic $Ti(NMe_2)_4$ and application of the amine elimination approach led to the desired bis(amido)cyclodiphosph(III)azane titanium(IV) dichloro complexes $[(RN)(t\text{BuNP})]_2TiCl_2$ (**12**−**15**) in high yield. According to the ^{31}P NMR spectra, the titanium(IV)-amido bonds in these complexes have covalent character.

MAO activated titanium(IV)dichloride complexes $[(RN)(t\text{BuNP})]_2TiCl_2$ (**12**−**15**) display moderate ethene polymerization activity. The polymerization behavior depends on the bulkiness of the ligand substituents. Large alkyl and aryl groups both protect the catalytically-active site from side reactions and prevent the phosphorus atoms of the ligand from destructive MAO coordination. Complex $[(t\text{BuN})(t\text{BuNP})]_2TiCl_2$ (**10**), bearing *t*Bu groups, exhibits an initially high polymerization activity, but ethene consumption falls off sharply after just a few minutes. $[(RN)(t\text{BuNP})]_2TiCl_2$ **12**−**15** produce very high molar mass polyethylene with a relatively narrow molar mass distribution. The bulky aromatic groups in **12**−**15** protect the metal center, which is seen in the slow decline of the catalytic activity during prolonged polymerization. The series of catalysts described here offers an efficient route toward very high or even ultrahigh molar mass linear polyethene. The focus of our future research is to introduce other early transition metals into the coordination chemistry of bis(amino)cyclodiphosph(III)azanes so as to enhance their catalytic performance.

Experimental Section

General Remarks: All manipulations were performed under an argon atmosphere using standard Schlenk techniques. The hydrocarbon and ethereal solvents were boiled under reflux over sodium and benzophenone, distilled, and stored under an inert atmosphere with pieces of sodium. Dichloromethane was boiled under reflux with CaH_2 powder and distilled before use. Mass spectra were measured on a JEOL SX102 spectrometer and the ^1H and ^{13}C

NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. The ^1H and ^{13}C NMR spectra are referenced relative to $CHCl_3$ (δ = 7.24 and 77.0 ppm, respectively) or C_6D_5H (δ = 7.15 and 128.0 ppm, respectively). ^{31}P NMR spectra were collected with a Bruker AMX 400 spectrometer, with phosphorus signals referenced to an external 85 % H_3PO_4 solution. Elemental analyses were performed Analytische Laboratorien Prof. Dr. H. Malissa and G. Reuter GmbH, Lindlar, Germany. High-temperature gel permeation chromatography of polyethylene samples (GPC) was performed in 1,2,4-trichlorobenzene at 145 °C by using a Waters HPLC 150 C.

tert-Butylamine and phosphorus trichloride were purchased from Merck and purified by distillation under argon (*t*BuNH$_2$ over sodium hydroxide). Arylamines and diphenylmethylamine were obtained from Aldrich and distilled in vacuo over sodium hydroxide before use. Chlorotrimethylsilane was purchased from Fluka and used as received. Ti(NMe$_2$)$_4$ was purchased from Aldrich and used as solution in toluene. Methylalumoxane (MAO, 30 wt.% solution in toluene) was received from Borealis Polymers Oy. *cis*-[Cl(*t*BuNP)]$_2$ (**1**),[16] *cis*-[(*t*BuNH)(*t*BuNP)]$_2$,[21] *cis*-[(C$_6$H$_5$NH)(*t*BuNP)]$_2$ [12] and *cis*-[(*t*BuN)$_2$(*t*BuNP)$_2$]Li$_2$(THF)$_2$ [21] were prepared according to modified literature procedures.

***cis*-[(2,6-*i*Pr$_2$C$_6$H$_3$NH)(PN-*t*Bu)]$_2$ (2):** 2,6-Diisopropylaniline (5.5 mL, 5.15 g, 29 mmol) and Et$_3$N (8.1 mL, 5.87 g, 58 mmol) were added to a stirred solution of *cis*-(ClPN-*t*Bu)$_2$ (**1**) (4 g, 14.5 mmol) in THF (100 mL) and the reaction mixture was boiled under reflux for four days. After filtration, all volatile compounds were removed under vacuum and pentane (20 mL) was added to the residue. The mixture was then kept in a freezer (−20 °C) overnight. After additional filtration and removal of pentane the required product was obtained as a colorless oil (6.42 g, 80 %). $C_{32}H_{54}N_4P_2$ (556.8): calcd. C 69.03, H 9.78, N 10.06; found C 69.65, H 9.88, N 9.31. ^1H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.17 (s, 18 H, *t*Bu), 1.27 (d, 24 H, C*H*$_3$, *i*Pr), 2.90 (m, 4 H, C*H*, *i*Pr), 4.63 (s, 2 H, N*H*), 7.05−7.18 (m, 6 H, Ar*H*) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 24.2 (*C*H$_3$, *i*Pr), 29.2 (m, *C*H, *i*Pr), 31.4 (t, *C*H$_3$C), 51.7 (t, CH$_3$*C*), 118.8 (Ar), 124.0 (Ar), 136.3 (Ar), 141.0 (d, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]benzene, 21 °C): δ_P = 114.8 (s) ppm. MS(EI): *m*/*z* (%) = 556 (48) [M$^+$], 380 (84), 204 (35), 176 (76), 57 (87).

***cis*-[(2-*t*BuC$_6$H$_4$NH)(PN-*t*Bu)]$_2$ (3):** Reaction of *cis*-(ClPN-*t*Bu)$_2$ (**1**) (0.65 g, 2.4 mmol), Et$_3$N (1.4 mL, 1.93 g, 9.6 mmol) and 2-*tert*-butylaniline (0.75 mL, 0.71 g, 4.7 mmol) and separation of the resulting crude product were carried out as for **2**. The obtained white solid was dissolved in pentane (10 mL) and the solution was concentrated to 3 mL and kept at −20 °C until colorless crystals appeared (0.90 g, 76 %). Crystals suitable for X-ray crystallography were obtained in this manner. $C_{28}H_{46}N_4P_2$ (500.6): calcd. C 67.17, H 9.26, N 11.19, P 12.37; found C 66.99, H 9.33, N 11.06, P 12.47. ^1H NMR (200 MHz, CDCl$_3$, 29 °C): δ_H = 1.29 (s, 18 H, *t*Bu), 1.50 (s, 18 H, *t*BuAr), 5.34 (br.s, 2 H, N*H*), 6.80 (td, 2 H, Ar*H*, ^1J = 7.8, ^2J = 1.5 Hz), 7.12 (t, 2 H, Ar*H*, ^1J = 7.8, ^2J = 1.5 Hz), 7.30 (dd, 2 H, Ar*H*, ^1J = 8.0, ^2J = 1.5 Hz), 7.71 (d, 2 H, Ar*H*, *J* = 8.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CDCl$_3$, 29 °C): δ_C = 31.1 (t, *C*H$_3$C, $J_{P,C}$ = 6.7 Hz), 30.6 (*C*H$_3$CAr), 34.2 (CH$_3$*C*Ar), 51.5 (t, CH$_3$*C*, $J_{P,C}$ = 13.7 Hz), 115.9 (Ar), 116.5 (Ar), 119.3 (Ar), 126.7 (Ar), 133.6 (Ar), 141.8 (d, Ar, *J* = 11.0 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 97.8 (s) ppm. MS(EI): *m*/*z* (%) = 500 (58) [M$^+$], 364 (94), 203 (10), 162(32), 57 (99).

***cis*-[(2-CF$_3$C$_6$H$_4$NH)(PN-*t*Bu)]$_2$ (4):** Reaction of *cis*-(ClPN-*t*Bu)$_2$ (**1**) (2.6 g, 9.5 mmol), Et$_3$N (5.3 mL, 3.80 g, 37.8 mmol) and 2-trifluoromethylaniline (2.4 mL, 3.05 g, 18.9 mmol) and separation of the obtained crude product were carried out as above. The resulting white solid was dissolved in pentane (20 mL). This solution was then concentrated to 8 mL and kept at −20 °C to yield colorless crystals of product (4.20 g; 85 %). Crystals suitable for X-ray crystallographic analysis were obtained in this manner. $C_{22}H_{28}F_2N_4P_2$ (524.4): calcd. C 50.39, H 5.38, N 10.68, P 11.81; found C 49.46, H 5.91, N 10.89, P 11.88. ^1H NMR (200 MHz, CDCl$_3$, 29 °C): δ_H = 1.29 (s, 18 H, *t*Bu), 5.49 (br.s, 2 H, N*H*), 6.90 (t, 2 H, Ar*H*, *J* = 7.7 Hz), 7.38 (t, 2 H, Ar*H*, *J* = 8.0 Hz), 7.48 (dd, 2 H, Ar*H*, ^1J = 7.7, ^2J = 1.4 Hz), 7.66 (d, 2 H, Ar*H*, *J* = 7.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CDCl$_3$, 29 °C): δ_C = 30.9 (t, *C*H$_3$C, $J_{P,C}$ = 6.5 Hz), 51.6 (t, CH$_3$*C*, $J_{P,C}$ = 12.5 Hz), 116.4 (*C*CF$_3$, $J_{C,F}$ = 29.0 Hz), 116.9 (Ar), 117.4 (Ar), 119.2 (Ar), 126.6 (q, Ar, $J_{C,F}$ = 5.0 Hz), 132.71 (Ar), 124.5 (q, *C*F$_3$, $J_{C,F}$ = 272.0 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 107.8 (s) ppm. MS(EI): *m*/*z* (%) = 524 (37) [M$^+$], 364 (94), 203(10), 161(32).

***cis*-[(2,5-*t*Bu$_2$C$_6$H$_3$NH)(PN-*t*Bu)]$_2$ (5):** 2,5-Di-*tert*-butylaniline (3.88 g, 18.9 mmol), *cis*-(ClPN-*t*Bu)$_2$ (**1**) (2.60 g, 9.5 mmol) and Et$_3$N (5.3 mL, 3.83 g, 37.8 mmol) were mixed in THF (80 mL) and then boiled under reflux for four days. After filtration, all volatile compounds were removed under vacuum. The resulting white solid was dissolved in CH$_2$Cl$_2$ (15 mL) and hexane (30 mL) was added. The resulting solution was then kept at 0 °C overnight. The suspension that formed was filtered off and all volatile components were removed from the filtrate. The white solid product was then recrystallized from CH$_2$Cl$_2$/hexane solution at −20 °C (colorless crystals; 3.94 g; 68 %). Crystals suitable for the X-ray analysis were obtained in this manner. $C_{36}H_{62}N_4P_2$ (612.9): calcd. C 70.55, H 10.20, N 9.14, P 10.11; found C 70.39, H 10.34, N 8.96, P 10.30. ^1H NMR (200 MHz, CDCl$_3$, 29 °C): δ_H = 1.33 (s, 18 H, *t*Bu), 1.30 (s, 18 H, *t*BuAr), 1.48 (s, 18 H, *t*BuAr), 5.30 (br.d, 2 H, N*H*, *J* = 7.0 Hz), 6.80 (dd, 2 H, Ar*H*, ^1J = 8.4, ^2J = 2.2 Hz), 7.20 (d, 2 H, Ar*H*, *J* = 8.4 Hz), 7.80 (dd, 2 H, Ar*H*, ^1J = 5.5, ^2J = 2.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CDCl$_3$, 29 °C): δ_C = 30.7 (*C*H$_3$CAr), 31.2 (t, *C*H$_3$C, $J_{P,C}$ = 6.8 Hz), 31.3 (*C*H$_3$CAr), 33.8 (CH$_3$*C*Ar), 34.3 (CH$_3$*C*Ar), 51.4 (t, CH$_3$*C*, $J_{P,C}$ = 13.5 Hz), 113.4 (Ar), 114.1 (Ar), 116.0 (Ar), 126.2 (Ar), 130.8 (Ar), 141.7 (d, Ar, *J* = 9.9 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 98.1 (s) ppm. MS(EI): *m*/*z* (%) = 612 (18) [M$^+$], 408 (96), 204(10), 57 (38).

***cis*-[(Ph$_2$CHNH)(PN-*t*Bu)]$_2$ (6):** The reaction of diphenylmethylamine (2.5 mL, 2.67 g, 18.9 mmol), *cis*-(ClPN-*t*Bu)$_2$ (**1**) (2.0 g, 7.3 mmol) and Et$_3$N (4.1 mL, 2.94 g, 29.1 mmol) and the separation of the crude product were carried out as for **5**. The resulting white solid was then dissolved in CH$_2$Cl$_2$ (20 mL), and hexane (20 mL) was added to give a solution that was kept at 0 °C overnight. The precipitate that formed was filtered off and solvents from the filtrate were removed. The white solid product was then recrystallized from CH$_2$Cl$_2$/hexane solution as colorless crystals (3.94 g; 72 %). $C_{34}H_{42}N_4P_2$ (568.7): calcd. C 71.81, H 7.44, N 9.85; found C 71.64, H 7.34, N 9.77. ^1H NMR (200 MHz, CDCl$_3$, 29 °C): δ_H = 0.97 (s, 18 H, *t*Bu), 3.44 (dd, 2 H, Ph$_2$C*H*), 5.60 (dd, 2 H, N*H*), 7.18 (m, 20 H, Ar*H*) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CDCl$_3$, 29 °C): δ_C = 30.5 (t, *C*H$_3$C), 51.6 (t, CH$_3$*C*), 59.7 (Ph$_2$*C*H), 126.8 (Ar), 127.3 (Ar), 128.3 (Ar), 145.5 (d) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 100.0 (br. s) ppm. MS(EI): *m*/*z* (%) = 568 (72) [M$^+$], 403 (48), 386 (95), 204(20), 183(99), 167 (98), 77 (47), 57 (32).

***cis*-[(2,4-Me$_2$C$_6$H$_3$NH)(PN-*t*Bu)]$_2$ (7):** Reaction of *cis*-(ClPN-*t*Bu)$_2$ (**1**) (5.15 g, 18.7 mmol), (11 mL, 7.58 g, 75 mmol) and 2,4-dimethylaniline (4.6 mL, 4.54 g, 37.4 mmol) and separation of the crude product were carried out as described for compound **2**. The crude

product was then dissolved in pentane (20 mL) to give a solution that was kept in a freezer (−20 °C) overnight. After filtration and removal of solvent a colorless oil was obtained (7.46 g, 90 %) and used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 1.32 (s, 18 H, *t*Bu), 2.15 (s, 6 H, CH_3Ar), 2.27 (s, 6 H, CH_3Ar), 4.91 (br.d, 2 H, N*H*, *J* = 5.5 Hz), 6.96 (d, 4 H, Ar*H*), 7.50 (d, 2 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 17.8 (*C*H_3Ar), 20.5 (*C*H_3Ar), 31.0 (t, *C*H_3C, $J_{P,C}$ = 6.5 Hz), 51.7 (t, CH_3*C*, $J_{P,C}$ = 13.7 Hz), 115.0 (Ar), 117.7 (Ar), 125.0 (Ar), 127.0 (Ar), 131.2 (Ar), 139.0 (d, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ_P = 99.0 (s) ppm.

***cis*-[(2,6-Et$_2$C$_6$H$_3$NH)(PN-*t*Bu)]$_2$ (8):** This was prepared in the same manner as **7**, starting from *cis*-(ClPN-*t*Bu)$_2$ (**1**) (2.6 g, 9.5 mmol), Et_3N (5.3 mL, 3.83 g, 37.8 mmol), and 2,6-diethylaniline (3.1 mL, 2.82 g, 18.9 mmol). A colorless oil (4.47 g; 94 %) was obtained and used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 1.38 (s, 18 H, *t*Bu), 1.50 (t, 12 H, CH_3, Et), 3.13 (q, *J* = 7.7 Hz, 8 H, CH_2, Et), 4.86 (s, 2 H, N*H*), 6.80−7.50 (m, 6 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 15.3 (*C*H_3, Et), 26.7 (*C*H_2, Et), 31.8 (t, *C*H_3C, $J_{P,C}$ = 6.5 Hz), 52.1 (t, CH_3*C*, $J_{P,C}$ = 13.4 Hz), 123.2 (Ar), 130.0 (Ar), 136.1 (Ar), 141.2 (d, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ_P = 114.2 (s) ppm. MS (EI): *m*/*z* (%) = 500 (64) [M$^+$], 352 (83), 204 (20), 177(99), 57 (99).

[(2,4-Di-MeC$_6$H$_3$N)(*t*BuNP)]$_2$Li$_2$(THF)$_2$ (9): A solution of *n*BuLi in hexane (23 mL, 1.6 M, 35.5 mmol) was added dropwise to a stirred solution of **7** (7.46 g, 16.8 mmol) in THF (60 mL) at −30 °C. The reaction mixture was then stirred 20 min at −20 °C, allowed to warm to room temperature, and boiled under reflux for 5 h. The resulting yellow solution was then concentrated to 15 mL and pentane (40 mL) was added. This suspension was then stored overnight at −20 °C to give a white-yellow precipitate that was then separated and washed with several portions of pentane at −20 °C. The mother liquid was then concentrated to 8 mL and pentane (20 mL) was added. After two days at −20 °C a second lot of the white-yellow product was obtained (8.5 g in total; 84 %). Crystals suitable for X-ray analysis were obtained by crystallization from a THF/hexane mixture at −20 °C. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.16 (m, 8 H, THF), 1.54 (s, 18 H, *t*Bu), 2.41 (d, 12 H, CH_3, Ar), 3.28 (m, 8 H, THF), 7.20 (m, 4 H, Ar*H*), 7.80 (d, *J* = 7.9 Hz, 2 H, Ar*H*) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 20.5 (*C*H_3, Ar), 23.1 (*C*H_3, Ar), 25.3 (THF), 30.7 (t, *C*H_3C, $J_{P,C}$ = 7.60 Hz), 53.3 (t, CH_3*C*, $J_{P,C}$ = 16.0 Hz), 68.3 (THF), 116.72 (Ar), 118.5 (Ar), 124.3 (Ar), 127.2 (Ar), 133.8 (Ar), 142.1 (d, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene, 21 °C): δ_P = 163.01 (s) ppm.

[(*t*BuN)(*t*BuNP)]$_2$TiCl$_2$ (10): $TiCl_4$ (1.3 g, 0.75 mL, 6.84 mmol) was added dropwise to a solution of *cis*-[(*t*BuN)(*t*BuNP)]$_2$Li$_2$(THF)$_2$ (3.45 g, 6.84 mmol) in toluene at 0 °C. The reaction mixture was then stirred at 0 °C for 20 min and boiled under reflux overnight. The resulting brown suspension was filtered off and toluene was removed in vacuo. The obtained brown solid residue was then dissolved in CH_2Cl_2 (30 mL), and hexane was added until precipitation commenced. The solution then was cooled to −20 °C and left overnight. The resulting suspension was filtered through Celite and the solvents were removed. After a second recrystallization, an orange-brown powder (1.61 g; 50.6 %) was isolated. $C_{16}H_{36}Cl_2N_4P_2Ti$ (465.2): calcd. C 41.31, H 7.80; found C 41.58, H 8.01. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.23 (s, 18 H, *t*Bu, P_2N_2 cycle), 1.66 (s, 18 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 28.3 (t, $J_{P,C}$ = 7.25 Hz, *C*H_3, *t*Bu, P_2N_2 cycle), 33.7 (d, $J_{P,C}$ = 12.2 Hz, *C*H_3, *t*Bu), 54.6 (t, $J_{P,C}$ = 9.9 Hz, *C*, *t*Bu, P_2N_2 cycle), 60.2 (d, $J_{P,C}$ = 19.2 Hz, *C*, *t*Bu) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ_P = 117.4 (s) ppm. The complex was prepared earlier by a different procedure and the data given here are in good agreement with those reported.[21] MS(EI): *m*/*z* (%) = 465 (80) [M$^+$], 429 (40) [M$^+$ − Cl], 352 (98, ligand).

[(PhN)(*t*BuNP)]$_2$Ti(NMe$_2$)$_2$ (11a): A solution of Ti(NMe$_2$)$_4$ (1.3 g, 5.8 mmol) in toluene (10 mL) was added dropwise to a stirred solution of *cis*-[(PhNH)(*t*BuNP)]$_2$ (2.15 g, 5.5 mmol) in toluene (30 mL). The reaction mixture was then boiled under reflux overnight. All volatile components were removed in vacuo. The resultant red−brown residue was extracted with several portions of hexane. The extracts were then filtered, concentrated to 10 mL, and cooled to −20 °C to yield the product (1.34 g; 46.4 %) as a red-brown, crystalline solid. Crystals suitable for X-ray analysis were obtained by crystallization from hexane at −20 °C. $C_{24}H_{40}N_6P_2Ti$ (522.5): calcd. C 55.18, H 7.72, N 16.09; found C 55.53, H 8.00, N 15.53. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H = 1.50 (s, 18 H, *t*Bu), 3.43 (s, 12 H, NMe$_2$), 7.03 (t, *J* = 7.33 Hz, 2 H, *p*-H-Ph) 7.20−7.50 (m, Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C = 29.3 (t, $J_{P,C}$ = 7.2 Hz, *C*H_3, *t*Bu), 44.0 (NMe$_2$), 53.1 (t, $J_{P,C}$ = 11.1 Hz, *C*, *t*Bu), 117.7 (d, Ar), 119.5 (Ar), 128.6 (Ar), 151.0 (d, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ_P = 142.2 (s) ppm. MS(EI): *m*/*z* (%) = 522 (50) [M$^+$], 478 (64, M$^+$ − NMe$_2$), 434 (70, M$^+$ − 2NMe$_2$), 388 (90, ligand).

[(Ph$_2$CHN)(*t*BuNP)]$_2$TiCl$_2$ (12): *cis*-[(Ph$_2$CHNH)(*t*BuNP)]$_2$ (**6**) (2.23 g, 3.93 mmol) was dissolved in toluene and added via a syringe to a solution of Ti(NMe$_2$)$_4$ (0.87 g, 3.9 mmol) at 0 °C. The resultant mixture was boiled under reflux for 22 h to give the bis-dimethylamido titanium(IV) complex [(Ph$_2$CHN)(*t*BuNP)]$_2$-Ti(NMe$_2$)$_2$ (**12a**), which was analyzed by ^{1}H, ^{13}C and ^{31}P NMR. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.22 (s, 18 H, *t*Bu), 1.82−2.40 (12 H, N*Me*$_2$), 3.54 (dd, 2 H, *J* = 14.0 Hz, C*H*, Ph$_2$CH), 7.11 (m, 16 H, *o*- and *m*-Ph), 7.25 (d, *J* = 7.1 Hz, 4 H, *p*-H-Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 30.9 (t, $J_{P,C}$ = 7.2 Hz, *C*H_3C), 43.0 (NMe$_2$) 52.0 (t, $J_{P,C}$ = 15.0 Hz, CH_3*C*), 59.3 (d, *J* = 13.0 Hz, Ph$_2$*C*H), 126.8 (Ar), 127.7 (Ar), 128.6 (Ar), 146.1 (d, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ_P = 103.8 (s) ppm.

Subsequently, to form the dichloride, an excess of Me_3SiCl (5.2 mL, 4.48 g, 41.2 mmol) was added and the reaction mixture was stirred overnight at room temperature. The solvent was then removed and the product purified similarly to **10**, washed with pentane and dried in vacuo. The product was isolated as a brown powder (2.13 g, 72 %). $C_{34}H_{40}Cl_2N_4P_2Ti{\cdot}C_5H_{12}$ (757.6): calcd. C 61.83, H 6.92, N 7.40; found C 62.47, H 6.60, N 8.04. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.20 (s, 18 H, *t*Bu), 3.50 (dd, 2 H, *J* = 14.1 Hz, C*H*, Ph$_2$CH), 7.00 (t, *J* = 7.3 Hz, 8 H, *o*-H-Ph), 7.10 (t, *J* = 7.4 Hz, 8 H, *m*-H-Ph), 7.27 (d, *J* = 7.7 Hz, 4 H, *p*-H-Ph) ppm ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 30.8 (t, $J_{P,C}$ = 7.0 Hz, *C*H_3, *t*Bu), 52.0 (t, $J_{P,C}$ = 14.3 Hz, *C*, *t*Bu), 59.0 (Ph$_2$*C*H), 109.0 (Ar), 126.8 (Ar), 128.6 (Ar), 146.1 (Ar) ppm ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 21 °C): δ_P = 100.0 (s) ppm. MS (EI): *m*/*z* (%) = 684 (10) [M$^+$], 649 (15) [M$^+$ − Cl], 568 (95, ligand).

[(2,6-Et$_2$C$_6$H$_3$N)(*t*BuNP)]$_2$TiCl$_2$ (13): *cis*-[(2,6-Et$_2$C$_6$H$_3$NH)(*t*-BuNP)]$_2$ (**8**) (1.79 g, 3.58 mmol) in toluene and a toluene solution of Ti(NMe$_2$)$_4$ (0.8 g, 3.57 mmol) were treated as described above. To this solution Me_3SiCl (4.8 mL, 4.15 g, 38.2 mmol) was added and the reaction mixture was stirred overnight at room temperature. The solvent was removed then under vacuum to give a red-brown residue that was extracted first with hexane (30 mL) and then twice with a mixture of hexane (20 mL) and CH_2Cl_2 (7 mL).

After filtration and evaporation of solvent, the product was dried in vacuo to give a red-brown oil (1.9 g, 86.4 %). $C_{28}H_{44}Cl_2N_4P_2Ti$ (617.4): calcd. C 54.47, H 7.18, N 9.07; found C 54.08, H 7.41, N 9.51. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.41 (s, 18 H, *t*Bu), 1.45 (t, 12 H, C*H*$_3$, Et), 3.16 (q, *J* = 7.3 Hz, 8 H, C*H*$_2$, Et), 7.10−7.40 (6 H, H−Ar) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 14.9 (*C*H$_3$, Et), 26.3 (d, *J* = 9.9 Hz, *C*H$_2$, Et), 31.2 (t, $J_{P,C}$ = 6.5 Hz, *C*H$_3$, *t*Bu), 51.5 (t, $J_{P,C}$ = 14.5 Hz, *C,* *t*Bu), 123.3 (Ar), 127.1 (Ar), 135.7 (Ar), 138.1 (t, *J* = 1.9 Hz, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 114.6 (s) ppm. MS(EI): *m*/*z* (%) = 617 (55) [M$^+$], 583 (8) [M$^+$ − Cl], 500 (76, ligand).

[(2,6-*i*Pr$_2$C$_6$H$_3$N)(*t*BuNP)]$_2$TiCl$_2$ (14): A toluene solution of *cis*-[(2,6-*i*Pr$_2$C$_6$H$_3$NH)(*t*BuNP)]$_2$ (**2**) (3.65 g, 6.56 mmol) and Ti(NMe$_2$)$_4$ (1.47 g, 6.55 mmol) were treated as described above. The titanium(IV) bis-amido complex, generated in situ, [(2,6-*i*Pr$_2$C$_6$H$_3$N)(*t*BuNP)]$_2$Ti(NMe$_2$)$_2$ (**14a**) was then characterized by ^{1}H, ^{13}C, and ^{31}P NMR. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.32 (s, 18 H, *t*Bu), 1.39 (d, 24 H, C*H*$_3$, *i*Pr), 3.00−3.23 (12 H, N*Me*$_2$), 3.91 (m, 4 H, C*H,* *i*Pr), 6.90−7.30 (6 H, H-Ar) ppm ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 24.2 (*C*H$_3$, *i*Pr), 31.4 (t, $J_{P,C}$ = 6.5 Hz, *C*H$_3$, *t*Bu), 33.6 (d, *J* = 1 Hz, *C*H, *i*Pr), 45.7 (N*Me*$_2$), 51.6 (t, $J_{P,C}$ = 14.7 Hz, *C,* *t*Bu), 123.0 (Ar), 123.9 (Ar), 136.3 (t, *J* = 1.9 Hz, Ar), 140.9 (Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 115.6 (s) ppm.

To obtain the dichloride complex, Me$_3$SiCl (9 mL, 7.47 g, 69 mmol) was added to the red-brown solution of [(2,6-*i*Pr$_2$C$_6$H$_3$N)(*t*BuNP)]$_2$Ti(NMe$_2$)$_2$ (**14a**) via syringe, and the reaction mixture was stirred overnight at room temperature. The so-obtained product was then purified similarly to **13** to afford a red-brown oil that was treated with Et$_2$O to give a red-brown solid after drying in vacuo (3.60 g, 81 %). $C_{32}H_{52}Cl_2N_4P_2Ti$ (673.5): calcd. C 57.07, H 7.78, N 8.32; found C 56.83, H 7.98, N 8.44. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.32 (s, 18 H, *t*Bu), 1.39 (d, 24 H, C*H*$_3$, *i*Pr), 3.88 (m, 4 H, C*H,* *i*Pr), 7.10−7.60 (6 H, H−Ar) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 24.2 (*C*H$_3$, *i*Pr), 31.4 (t, $J_{P,C}$ = 6.7 Hz, *C*H$_3$, *t*Bu), 32.1 (d, *J* = 1 Hz, *C*H, *i*Pr), 51.3 (t, $J_{P,C}$ = 14.5 Hz, *C,* *t*Bu), 122.5 (Ar), 124.0 (Ar), 130.7 (Ar), 140.9 (Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 115.6 (s) ppm. MS (EI): *m*/*z* (%) = 672 (10) [M$^+$], 639 (8) [M$^+$ − Cl], 556 (90, ligand).

[(2,5-*t*Bu$_2$C$_6$H$_3$N)(*t*BuNP)]$_2$TiCl$_2$ (15): A toluene solution of *cis*-[(2,5-*t*Bu$_2$C$_6$H$_3$NH)(*t*BuNP)]$_2$ (**5**) (2.73 g, 4.46 mmol) and Ti(NMe$_2$)$_4$ (1.0 g, 4.46 mmol) was treated in the same way as **13**. The resultant titanium(IV) bis-amido complex, generated in situ, [(2,5-*t*Bu$_2$C$_6$H$_3$N)(*t*BuNP)]$_2$Ti(NMe$_2$)$_2$ (**15a**) was characterized by ^{1}H, ^{13}C, and ^{31}P NMR. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.44 (s, 36 H, *t*BuAr), 1.57 (s, 18 H, *t*Bu), 3.19 (12 H, N*Me*$_2$), 6.98 (dd, J_1 = 6.2, J_2 = 2.1 Hz, 2 H, 4-H−Ph), 7.36 (2 H, 3-H−Ph), 8.23 (dd, J_1 = 3.1, J_2 = 2.1 Hz, 2 H, 2-H−Ph) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 31.0 (*C*H$_3$, 5-*t*BuAr), 31.3 (t, $J_{P,C}$ = 6.5 Hz, *C*H$_3$, *t*Bu), 31.5 (*C*H$_3$, 2-*t*BuAr), 33.1 (*C,* 5-*t*BuAr), 34.0 (*C,* 2-*t*BuAr), 45.2 (N*Me*$_2$), 51.7 (t, $J_{P,C}$ = 13.7 Hz, *C,* *t*Bu), 113.8 (Ar), 114.5 (Ar), 117.1 (Ar), 131.2 (Ar), 141.9 (Ar), 150.0 (t, *J* = 1.2 Hz, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 98.86 (s) ppm.

To obtain the dichloride complex, Me$_3$SiCl (5.9 mL, 5.09 g, 46.8 mmol) was added to the red-brown solution of [(2,5-*t*Bu$_2$C$_6$H$_3$N)(*t*BuNP)]$_2$Ti(NMe$_2$)$_2$ (**15a**) and the reaction mixture stirred overnight at room temperature. All volatiles were then removed in vacuo and the residue was extracted three times with a mixture of hexane (30 mL) and CH$_2$Cl$_2$ (10 mL). After removal of the solvent, the product was washed with several portions (each 10 mL) of cold pentane and dried. A red−brown powder (2.40 g, 73.8%) was isolated. $C_{36}H_{60}Cl_2N_4P_2Ti$ (729.7): calcd. C 59.26, H 8.29, N 7.68; found C 58.94, H 8.41, N 7.86. ^{1}H NMR (200 MHz, [D$_6$]benzene, 29 °C): δ_H = 1.39 (s, 36 H, *t*BuAr), 1.52 (s, 18 H, *t*Bu), 6.93 (dd, ^1J = 6.2, ^2J = 2.1 Hz, 2 H2 Hz, 4-H−Ar), 7.32 (2 H, 3-H−Ar), 8.17 (dd, ^1J = 3.1, ^2J = 2.1 Hz, 2 H, 2-H−Ar) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 29 °C): δ_C = 31.0 (*C*H$_3$, 5-*t*BuAr), 31.4 (t, $J_{P,C}$ = 6.0 Hz, *C*H$_3$, *t*Bu), 31.5 (*C*H$_3$, 2-*t*BuAr), 33.1 (*C,* 5-*t*BuAr), 34.5 (*C,* 2-*t*BuAr), 51.7 (t, $J_{P,C}$ = 13.7 Hz, *C,* *t*Bu), 113.8 (Ar), 114.5 (Ar), 117.1 (Ar), 131.1 (Ar), 137.8 (Ar), 150.0 (Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 21 °C): δ_P = 99.72 (s) ppm. MS (EI): *m*/*z* (%) = 728 (20) [M$^+$], 693 (10) [M$^+$ − Cl], 612 (40, ligand).

Polymerization Experiments: A 1-L glass autoclave (manufacturer Büchi) was charged with toluene (200 mL) and cocatalyst (MAO) (Al/Ti ratio was 1000), thermostatted (50 or 70 °C), saturated with ethene (3.8 bar), and the desired amount of complex solution was then added. The monomer pressure (±50 mbar) and temperature (±0.5 °C) were kept constant during each polymerization run. Monomer consumption, polymerization temperature and pressure were controlled by real-time monitoring. The polymerizations were quenched with 10 % HCl solution in methanol, and the polymer precipitated quantitatively by pouring the solution into methanol (400 mL) acidified with aqueous hydrochloric acid. The samples were washed several times with methanol and water, and dried at 60 °C.

X-ray Crystallographic Study: Crystal data of compounds **3**−**5** were collected with an Enraf−Nonius CAD-4 single-crystal diffractometer at 193(2) K using Cu-K_α radiation (graphite monochromator), 1.54179 Å (scan-type omega/2-theta). Intensities were corrected for Lorentz and polarization effects with XCAD4.[26,27]

The crystal data of compound **9** were collected with a Rigaku AFC-7S single-crystal diffractometer at 193(2) K using Mo-K_α radiation (graphite monochromator), 0.71073 Å (omega/2-theta scans). Intensities were corrected for Lorentz and polarization effects with TEXSAN.[28] A psi-scan absorption correction was made for each compound.[29]

The crystal data of compound **11a** were collected with a Nonius KappaCCD area-detector diffractometer at 173(2) K using Mo-K_α radiation (graphite monochromator), 0.71073 Å. Data reduction: COLLECT;[30] absorption correction: SADABS.[31]

Solution and refinement: SHELX-97,[32,33] direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions. The displacement factors of the H-atoms were 1.2× (1.5×) that of the host atom. Data relating to the structure determinations are collected in Table 5. CCDC-213508 to -213512 (for compounds **3**−**5**, **9**, **11a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 5. Crystallographic data for compounds **3**–**5**, **9**, **11a**

Compound	**3**	**4**	**5**	**9**	**11a**
Formula	$C_{28}H_{46}N_4P_2$	$C_{22}H_{28}F_6N_4P_2$	$C_{36}H_{62}N_4P_2$	$C_{36}H_{60}Li_2N_4O_3P_2$	$C_{24}H_{40}N_6P_2Ti$
Fw	500.63	524.42	612.84	672.70	522.46
Space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$C2/c$	$P2_1/c$
a, Å	10.130(1)	9.251(1)	9.885(1)	14.761(5)	11.903(1)
b, Å	18.899(1)	11.010(1)	18.136(1)	15.070(3)	22.667(2)
c, Å	15.907(1)	13.790(1)	21.012(1)	17.815(3)	11.699(1)
α, deg	90	81.44(1)	90	90	90
β, deg	98.19(1)	82.66(1)	90	98.94(2)	115.808(1)
γ, deg	90	69.440(10)	90	90	90
V, Å^3	3014.3(4)	1296.1(2)	3766.9(5)	3914.8(17)	2841.6(4)
$d_{calcd.}$, g cm^{-3}	1.103	1.344	1.081	1.141	1.221
Z	4	2	4	4	4
μ, cm^{-1}	14.60	20.73	12.45	1.48	0.436
λ, Å	1.54179	1.54179	1.54179	0.71073	0.71073
T, K	193(2)	193(2)	193(2)	193(2)	173(2)
R[a]	0.0675	0.0486	0.0433	0.0835	0.0613
R_w[b]	0.1911	0.1417	0.1158	0.2345	0.1434

[a] $R = \Sigma F_o - F_c/\Sigma F_o$ for observed reflections [$I > 2\sigma(I)$]. [b] $Rw = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.

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