Alkyl(amino)- and Alkyl(chloro)phosphanyl-Substituted Cyclopentadienyl Complexes of Titanium and Zirconium

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Dedicated to Prof. Dr. J. Lorberth on the occasion of his 65th birthday

Keywords: Titanium / Zirconium / Cyclopentadienyl ligands / P ligands / Polymerisation

Phosphanyl-substituted cyclopentadienes of the type [R_nCp–PR(NR^1R^2/Cl)] (**1**–**22**) (R = Alk, Ar; R^1, R^2 = H, Alk, Ar, SiR_3; R_nCp = *t*BuCp, Me_4Cp, Ind, Me_6Ind, Flu) can be synthesised by reaction of alkyldichlorophosphanes and alkyl(amino)chlorophosphanes with alkali metal cyclopentadienides. The method used is a general one and provides high isolated yields of the target compounds. The phosphanylcyclopentadienes can easily be deprotonated by strong bases (e.g. *n*BuLi, $PhCH_2K$, Ph_2CHK) and the potassium salts [R_nCp–PR(NR^1R^2)]K (**25**–**28**) are efficiently transmetallated by Me_3SnCl. A subsequent reaction with $TiCl_4(L)_2$ and $ZrCl_4(L)_2$ (L = THF, tetrahydrothiophene, Me_3P) affords new half-sandwich complexes [{Me_4Cp–P*t*Bu(NEt_2)}$TiCl_3$] (**36**), [{Me_4Cp–P*t*Bu(NEt_2)}$TiCl_3$] (**37**) and [{*t*BuCp–P*t*Bu(NEt_2)}$TiCl_3$] (**38**) in moderate yields. The reaction of [*t*BuCp–P*t*Bu(Cl)] (**6**) with $TiCl_4$ in the presence of Et_3N at low temperature yields the half-sandwich complex [{*t*BuCp–P*t*Bu(Cl)}$TiCl_3$] (**39**) quantitatively; [(Cp–P*t*Bu(Cl)]$_2$-CMe_2] (**11**) reacts similarly and gives, dependent on the reagent ratio, either the homobimetallic derivative [{(Cp–P*t*Bu(Cl)$_2$$CMe_2$}{$TiCl_3$}$_2$] (**40**) (1:2 ratio) or the *ansa* complex [{(Cp–P*t*Bu(Cl)]$_2$$CMe_2$}$TiCl_2$] (**41**) (1:1 ratio). The scope of this reaction could not be extended to sterically more demanding cyclopentadienyl derivatives. Treatment of [{*t*BuCp–P*t*Bu(Cl)}$TiCl_3$] (**39**) by LiN(H)*t*Bu in the presence of Et_3N leads to the formation of the constrained geometry complex [{*t*BuCp–P*t*Bu(N*t*Bu)}$TiCl_2$] (**42**) in a high yield. All synthesised compounds were characterised by NMR spectroscopy, mass spectrometry and elemental analyses. The crystal structures of the ligand precursor [Me_6Ind–P*t*Bu(NH*t*Bu)] (**15**) and that of [{Me_4Cp–P*t*Bu(NEt_2)}$TiCl_3$] (**36**) have been determined by X-ray diffractometry. The complexes described in this work are active in the MAO-mediated polymerisation of ethylene.

Introduction

In the past three decades a variety of transition metal complexes have been developed and applied as catalysts for homogeneous polymerisation of α-olefins to form a wide number of polymers with unique properties.[1−3] The most famous of them are *ansa*-metallocenes **I**[4] and *C*onstrained *G*eometry *C*atalysts (CGC) **II** with ancillary cyclopentadienyl ligands first described by Bercaw,[5] Okuda[6] and later developed by researchers of Dow and Exxon.[7] At the same time other systems, having no cyclopentadienyl-type ligands at all[8−11] were successfully applied for the homogeneous polymerisation of alkenes and have promoted extensive studies focussed on the catalyst geometry,[12−20] and investigation of the relationship between the catalyst's structure and properties of the polymer produced.[21,22] As a consequence, a huge number of theoretical[23,24] and experimental studies of the mechanism of polymerisation have been reported to date.[25−29] There is still growing interest in substituted cyclopentadienylmetal compounds containing a terminal donor group in the side chain.[11−19] Due to the Lewis acidity of the metal centre in the postulated active species in the polymerisation reaction a coordination of the "pendant" donor functionality to the transition metal centre might be anticipated.

We were interested in novel ligand models and the synthesis of transition metal complexes on their basis. Recently,

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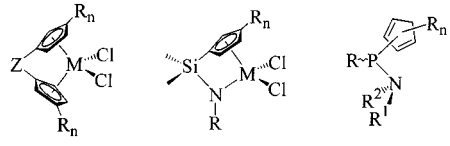
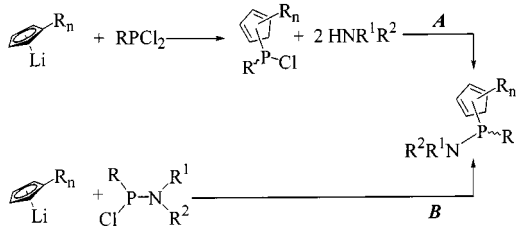
we have been exploring the synthesis of the ligands derived from phosphanyl-substituted cyclopentadienes [$R_nCp-PR(NR^1R^2)$] (**III**) (R_nCp = Cp, Ind, Flu; R, R^1, R^2 = Alk, Ar or H) in an attempt to probe this class of compounds in the organotransition metal chemistry. The choice of the [$R_nCp-PR(NR^1R^2)$] system was stimulated by the expectation that the presence of a σ-donating aminophosphanyl group in the periphery of the cyclopentadienyl ligand would have an impact on the catalytic properties of target complexes.



I **II** **III**

Z = carbon or silicon bridge; R_nCp = Cp, Ind, Flu; R, R^1, R^2 = Alk or Ar; M = Ti (IV), Zr (IV), Hf (IV).

There are two main synthetic approaches to these ligands of type **III** (Scheme 1) containing a three-coordinate phosphorus atom: ***A***) a stepwise nucleophilic substitution of the halogen atoms at the phosphorus centre of $RPCl_2$ by cyclopentadienyl-type carbanions [R_nCp]M (M = Li, Na, K) and amines HNR^1R^2 and ***B***) the reaction of cyclopentadienyl anions with (alkyl or aryl)chloro(dialkylamino)-phosphanes.



R_nCp = Cp, Ind, Flu; R = Alk, Ar; R^1 = H or R^2; R^2 = Alk or Ar.

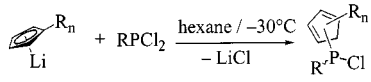
Scheme 1

Route ***A*** is a common route to prepare alkyl(amino)-cyclopentadienylphosphanes and has been described previously in the literature for pentamethylcyclopentadienes.[30] The second approach ***B*** for which alkyl(or aryl)chloro(dialkylamino)phosphanes $RP(Cl)NR^1R^2$ are key starting compounds has recently been developed.[31] They could be advantageously used for the preparation of sterically less encumbered derivatives. Here we wish to report the synthesis of the new phosphanylcyclopentadienes **III**, using route ***A*** as a synthetic strategy, their transformations to group-4 transition metal complexes and our results of the polymerisation of ethylene by the catalysts obtained from the complexes and methylalumoxane (MAO).

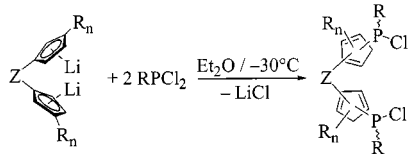
Results and Discussion

Synthesis of the Ligand Precursors

Phosphanylcyclopentadienes of the type [$R_nCp-PR(Cl)$] can be prepared by nucleophilic substitution of a chlorine atom in dichlorophosphanes $RPCl_2$ (Scheme 1, route ***A***). In the 1980s this synthetic approach was applied for a variety of pentamethylcyclopentadienylphosphanes [$Me_4C_5-PR^3R^4$] (R^3, R^4 = C_5Me_5(Cp*), Alk, Ar, Cl, F, I, NMe_2) with the aim of studying isomerisation of the phosphanyl substituent around the Cp* ring.[32−36] Sterically crowded cyclopentadienes, indenes, fluorenes, or bulky phosphanes can also be utilised while cyclopentadienylphosphanes having less demanding substituents, e.g. Cp or MeCp, are a thermally labile class of compounds and readily undergo Diels−Alder reaction.[37] The most recent examples were reported by Alt and co-workers[38] and by researchers at Shell[39] as intermediate compounds in the synthesis of symmetrical and unsymmetrical *ansa*-metallocenes with the phenylphosphanylidene bridge. In both cases subsequent nucleophilic substitutions by different cyclopentadienyl-, indenyl- and fluorenyllithium salts have been carried out. According to a similar methodology we synthesised a number of alkylchloro(cyclopentadienyl-, indenyl- and fluorenyl)phosphanes [$R_nCp-PR(Cl)$] (**1**−**6**) and their bridged analogues [{$R_nCp-PR(Cl)$}$_2$Z] (**7**−**11**) (Scheme 2).



[R_nCp-PR(Cl)] = **1** [Ind-P*t*Bu(Cl)] 66%
2 [Flu-P*t*Bu(Cl)] 94%[40]
3 [Ind-PMes(Cl)] 82%
4 [Me_6Ind-P*t*Bu(Cl)] 85%
5 [Me_4Cp-P*t*Bu(Cl)] 73%
6 [*t*BuCp-P*t*Bu(Cl)] 95%



[{R_nCp-PR(Cl)}$_2$Z] = **7** [{Ind-P*t*Bu(Cl)}$_2$(CH_2)$_2$] 64%
8 [{Ind-P*t*Bu(Cl)}$_2$$CMe_2$] >95%
9 [{Ind-P*t*Bu(Cl)}$_2$$CEt_2$] 92%
10 [{Ind-P*t*Bu(Cl)}CMe_2{Cp-P*t*Bu(Cl)}] 50%
11 [{Cp-P*t*Bu(Cl)}$_2$$CMe_2$] 80%

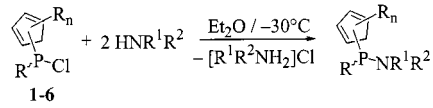
Scheme 2

This method, however, has some drawbacks. In the case of monocyclopentadienyl-type carbanions the formation of by-products is observed, e.g. alkylbis(cyclopentadienyl)phosphane [$(R_nCp)_2PR$], as a result of the double substitution of the chlorine atoms at the phosphorus centre, when Et_2O was used as solvent. By-products can be avoided by the use of a nonpolar aliphatic solvent, e.g. hexane. Since many compounds derived from phosphanylcyclopentadienes [$R_nCp-PR(Cl)$] or [$R_nCp-PR(NR^1R^2)$] cannot be purified

by standard methods such as distillation or chromatography, pure starting materials have to be used in all stages of the preparation. The substances synthesised are highly soluble in aliphatic solvents and exist as expected as mixtures of isomers (see NMR spectroscopic data in the Exp. Sect.).

On the contrary, bis[*tert*-butylchloro(indenyl)phosphanes] [{Ind−P*t*Bu(Cl)}$_2$Z] (**7**−**9**) exist exclusively as allylic regioisomers. These compounds possess four stereogenic centres and hence consist of a complex set of stereoisomers. Eight diastereomeric pairs are theoretically possible. Four of them would exhibit an identical chemical environment around the phosphorus substituents and only four diastereomers could therefore be observed by conventional NMR techniques (three enantiomeric pairs and one *meso* form).[31] The ^{31}P NMR spectroscopic data confirm this assumption and demonstrate seven resonances, i.e. three pairs of nonequivalent phosphorus atoms in the racemic forms and one signal of the *meso* form, each part having different integral intensity (compare ref.[31]). For this reason we were not able to make a detailed assignment of the proton and carbon NMR spectra for compounds **6**,**7**−**11**. The structures of **10** and **11** were deduced solely on the basis of C,H,N analyses and ^{31}P NMR spectra.

The second step of method ***A*** is the reaction of [R$_n$Cp−PR(Cl)] (**1**−**11**) with amines. This transformation proceeds smoothly for **1**−**6** and affords aminophosphanyl derivatives **12**−**22** in high yields (Scheme 3). The structure of [Me$_6$Ind−P(*t*Bu)N(H)*t*Bu] (**15**) was determined by an X-ray analysis (Figure 1).



1-6

[R$_n$Cp-PR(NR^{1}R^2)] =
12 [Ind-P*t*Bu(NEt$_2$)] >95%
13 [Ind-P*t*Bu(NH*t*Bu)] >95%
14 [Ind-P*t*BuP(NHPh)] >95%
15 [Me$_6$Ind-P*t*Bu(NH*t*Bu)] 75%
16 [Ind-PMes(NH*t*Bu)] >95%
17 [Flu-P*t*Bu(NEt$_2$)] >95%
18 [Flu-P*t*Bu(NH*t*Bu)] >95%
19 [Me$_4$Cp-P*t*Bu(NH*t*Bu)] 78%
20 [Me$_4$Cp-P*t*Bu(NEt$_2$)] >95%
21 [*t*BuCp-P*t*Bu(NEt$_2$)] >95%
22 [*t*BuCp-P*t*Bu(NH*t*Bu)] >95%

Scheme 3

The geometry at the phosphorus atom that occupies the allylic position of the Me$_6$Ind group is trigonal-pyramidal. The bond angles range from 103 to 108°, indicating certain steric strain in the molecule. The P(1)−N(1) bond of 1.701(5) Å and the bond P(1)−C(11) of 1.899(5) Å are somewhat longer than typical P^{III}−N (ca. 1.65 Å) and P^{III}−C (1.83−1.87 Å) bond lengths for most substituted organophosphorus compounds,[41] which again confirms the steric congestion in **15**. All other structural fragments reveal no peculiarities.

To our surprise, for the bridged ligand precursors [{R$_n$Cp−P*t*Bu(Cl)}$_2$Z] (**7**−**10**), no nucleophilic substitution by secondary amines HNR^{1}R^2 takes place. The reaction affords oligomeric products which are difficult to analyse,

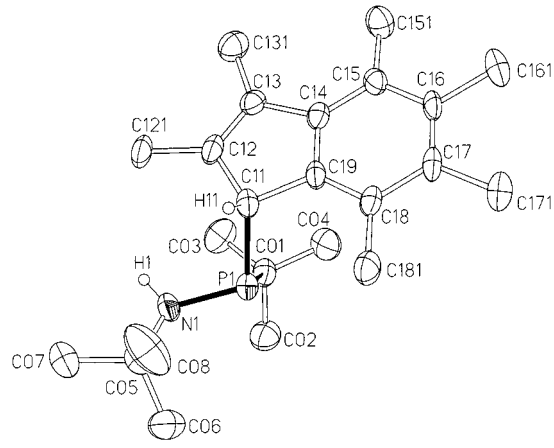
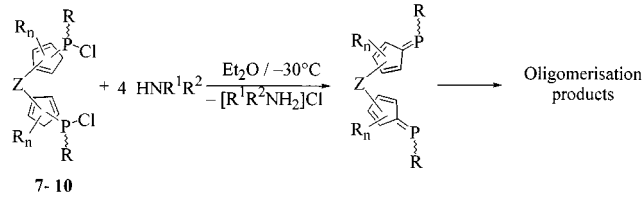


Figure 1. ORTEP diagram of the molecule of [Me$_6$Ind−P*t*Bu(NH*t*Bu)] (**15**); thermal ellipsoids are drawn at 50% probability level; hydrogen atoms except for H(1) and H(11) are omitted for the sake of clarity; selected bond lengths [Å]: P(1)−N(1) 1.701(5), P(1)−C(01) 1.880(6), P(1)−C(11) 1.899(5), C(11)−C(12) 1.504(8), C(11)−C(19) 1.518(7), C(12)−C(13) 1.350(8); selected bond angles [°]: N(1)−P(1)−C(01) 102.5(2), N(1)−P(1)−C(11) 103.3(2), C(01)−P(1)−C(11) 108.0(2), C(19)−C(11)−P(1) 112.7(3), C(13)−C(12)−C(11) 110.9(5)

probably stemming from the very reactive phosphafulvenes generated in situ by β-"HCl" elimination.[42] Thus, the elimination of HCl takes place faster than a nucleophilic substitution reaction (Scheme 4).



7- 10

HNR^{1}R^2 = HNMe$_2$, HNEt$_2$, HN(*i*Pr)$_2$, H$_2$N(*t*Bu); Z = -(CH$_2$)$_2$-, CMe$_2$.

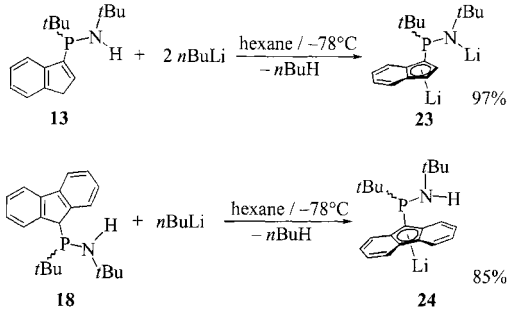
Scheme 4

The result of the reaction is independent of the length of the bridge Z and the size of alkyl groups R^1 and R^2, which might be attributed to an exclusively allylic structure of the bis[alkylchloro(indenyl)phosphanes] [{R$_n$Cp−P*t*Bu(Cl)}$_2$Z] (**7**−**10**) and/or higher steric hindrance in these encumbered substrates. Bis[alkylchloro(indenyl)phosphane] **11**, isolated as a mixture of allylic and vinylic isomers, gave, after the addition of the amine HNR^{1}R^2 a mixture of the desired products formed from the vinylic isomer and oligomers derived from the allylic isomer. The attempts to separate these substances were unsuccessful. Luckily, such ligand precursors are available by synthetic route ***B*** and can readily be obtained in high yield.[31]

Syntheses of the Complexes

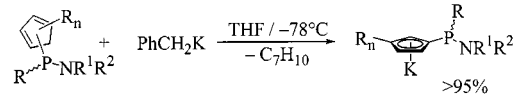
Taking into account the geometry of the prepared ligand precursors several types of transition metal complexes might be synthesised: half-sandwich, sandwich, CGC (**II**) and *ansa*-type (**I**) metallocenes. To date, a variety of methods for the preparation of such early transition metal complexes has been described in the literature.[43] The most

common synthetic approach to the desired compounds is the transmetallation reaction between transition metal halides and alkali metal derivatives of the ligands. The lithium salts **23** and **24** were prepared in order to be further treated with transition metal halides. After **13** and **18** have been treated with *n*BuLi in 2:1 and 1:1 ratios, respectively, the corresponding di- and monolithium salts are formed (Scheme 5).



Scheme 5

The compounds **23** and **24** are soluble in aliphatic solvents, thus making purification difficult. Potassium salts are expected to be less soluble and a series was synthesised by the use of Ph_2CHK or $PhCH_2K$ as deprotonating agents in THF (Scheme 6).



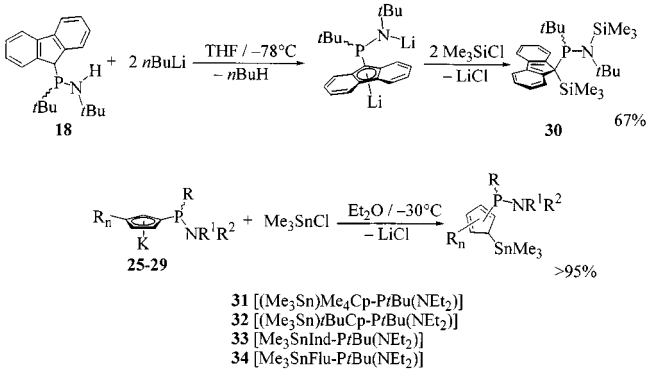
12, **17**, **18**, **20**, **21**

$[R_nCp\text{-}PR(NR^1R^2)]K$ = **25** [Me_4Cp-P*t*Bu(NEt_2)]K
26 [*t*BuCp-P*t*Bu(NEt_2)]K
27 [Ind-P*t*Bu(NEt_2)]K
28 [Flu-P*t*Bu(NEt_2)]K

$[\{R_nCp\text{-}PR(NR^1R^2)\}_2Z]K_2$ = **29** [$\{$Ind-P*t*Bu(NEt_2)$\}_2CEt_2]K_2(THF)_2$ 81%

Scheme 6

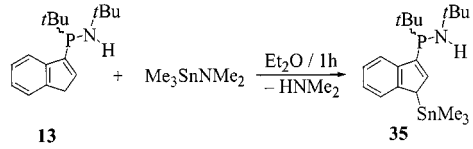
The salts **25**−**28** do not contain THF as a ligand and can be obtained free of any THF by washing with an aliphatic solvent. The alkali metal derivatives can then be transformed into the corresponding Me_3Si or Me_3Sn derivatives **30**−**34** (Scheme 7).



31 [(Me_3Sn)Me_4Cp-P*t*Bu(NEt_2)]
32 [(Me_3Sn)*t*BuCp-P*t*Bu(NEt_2)]
33 [Me_3SnInd-P*t*Bu(NEt_2)]
34 [Me_3SnFlu-P*t*Bu(NEt_2)]

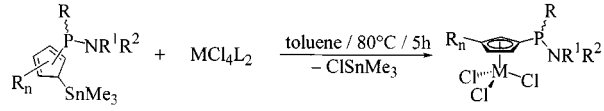
Scheme 7

The reaction of the ligand precursors with trialkyltin amides proceeds smoothly and results in *C*-stannylated products, e.g. when **13** is treated with 1 equiv. of Me_3SnNMe_2, **35** is formed quantitatively (Scheme 8). At room temperature Me_3Si and Me_3Sn groups occupy allylic positions of the cyclopentadienyl ring.



Scheme 8

Our numerous efforts to isolate desired complexes [half-sandwich, sandwich, CGC (**II**) and *ansa*-type (**I**)] of Ti^{IV} and Zr^{IV} from the reactions of homoleptic alkylmetal compounds (Alk = CH_2Ph), metal amides (NR_2 = NMe_2) of Ti^{IV}, Zr^{IV} and neutral ligand precursors **12**−**22** analogously to $R_nCpSiMe_2(NHtBu)$ (R_nCp = C_5H_5, Me_4C_5),[44] or between disilylated (**30**), dilithium/dipotassium (**23** and **29**), lithium/potassium (**24** and **25**−**28**) derivatives of the ligands and THF, THT (THT = tetrahydrothiophene) and Me_3P adducts of $TiCl_4$ and $ZrCl_4$, were unsuccessful. Either no reaction took place over rational periods of time, or complex mixtures of products were formed, which were difficult to separate and identify. The method of choice is the reaction of trimethyltin derivatives with $TiCl_4$ and $ZrCl_4$. Several substituted alkyl(amino)cyclopentadienylphosphanes [(Me_3Sn)R_nCp−P*t*Bu(NR^1R^2)] (**31**, **32**) and several Ti^{IV} (**36**, **38**) and Zr^{IV} (**37**) complexes have been synthesised in moderate yields (Scheme 9).



$[\{R_nCp\text{-}PR(NR^1R^2)\}MCl_3]$ = **36** [$\{Me_4Cp$-P*t*Bu(NEt_2)$\}TiCl_3$] 38%
37 [$\{Me_4Cp$-P*t*Bu(NEt_2)$\}ZrCl_3$] 25%
38 [$\{$*t*BuCp-P*t*Bu(NEt_2)$\}TiCl_3$] 30%
L = THF, THT, Me_3P.

Scheme 9

The main product of these reactions is a coordination polymer and the yield of the desired compound is not affected by donor molecules coordinated to the metal centre (THF, THT, Me_3P). In the case of indenyl- (**33**) and fluorenyltin (**34**) derivatives only ill-defined oligomeric products could be isolated. According to NMR spectroscopic data the oligomeric substance still contains the π-bound cyclopentadienyl ligand. The oligomeric products obtained from indenyl- and fluorenyl-containing phosphanes are soluble in polar solvents, e.g. CH_2Cl_2, toluene or THF, and decompose to $TiCl_3$ and presumably also the dimeric organic species formed from the ligand upon storage. Such behaviour is documented for situations when fluorenyltitanium complexes were attempted to be synthesised.[45] The complexes **36**−**38** are in turn very soluble in pentane and could be separated from the oligomers by extraction. Again, when a pentane solution of **36**−**38** was stored for several weeks at room temperature a precipitate containing decomposition products was formed.

Diffraction-quality crystals of [{$Me_4Cp-PtBu(NEt_2)$}$TiCl_3$] (**36**) and [{tBuCp−PtBu(NEt_2)}$TiCl_3$] (**38**) could be obtained from saturated *n*-pentane solutions at −80 °C, and a single-crystal X-ray structure of [{$Me_4Cp-PtBu(NEt_2)$}$TiCl_3$] (**36**) has been determined (Figure 2). The structure of **38** could not be solved due to twinning problems.

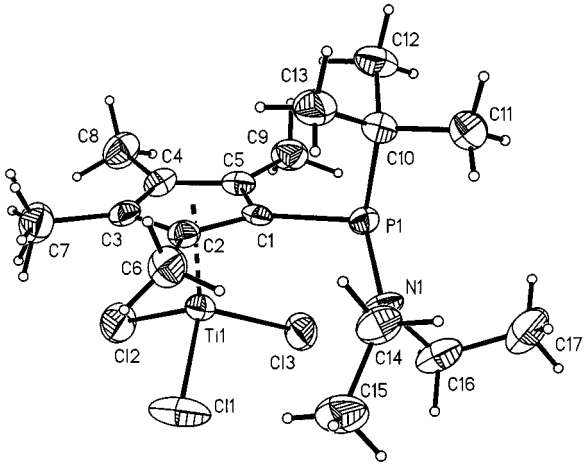
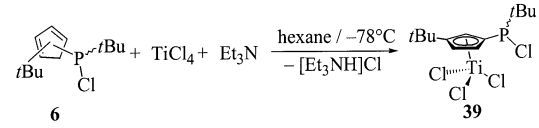


Figure 2. ORTEP diagram of the molecular structure of [{$Me_4Cp-PtBu(NEt_2)$}$TiCl_3$] (**36**); thermal ellipsoids are drawn at 50% probability level; selected bond lengths [Å]: Ti(1)−Cl(3) 2.232(2), Ti(1)−Cl(2) 2.235(2), Ti(1)−Cl(1) 2.235(2), Ti(1)−C(1) 2.328(5), Ti(1)−C(2) 2.352(5), Ti(1)−C(3) 2.368(5), Ti(1)−C(4) 2.379(5), Ti(1)−C(5) 2.339(5), P(1)−N(1) 1.691(4), P(1)−C(1) 1.862(6), P(1)−C(10) 1.897(6), N(1)−C(16) 1.465(7), N(1)−C(14) 1.479(7); selected bond angles [°]: Cl(1)−Ti(1)−Cl(2) 101.91(8), Cl(3)−Ti(1)−Cl(1) 104.47(8), Cl(3)−Ti(1)−Cl(2) 100.74(8), C(1)−P(1)−C(10) 100.3(2), N(1)−P(1)−C(1) 108.6(2), N(1)−P(1)−C(10) 110.4(2), C(16)−N(1)−C(14) 113.9(4), C(14)−N(1)−P(1) 128.7(4), C(16)−N(1)−P(1) 112.7(4); non-bonding distance [Å]: Ti(1)−N(1) 4.03

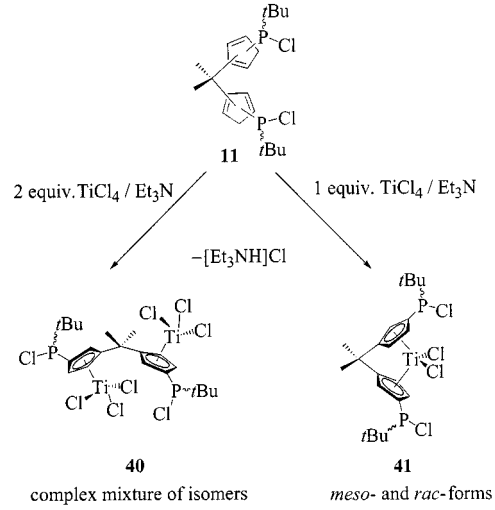
The racemic mixture of the chiral complex **36** crystallises in the centrosymmetric space group $P2_1/c$ building up non-chiral crystals. The coordination geometry at the titanium atom can be described as a piano-stool configuration typical for half-sandwich complexes, e.g. [$CpTiCl_3$].[46] The η^5-bound cyclopentadienyl ligand is practically planar with Ti−C bond lengths ranging from 2.332(2) to 2.379(5) Å and with C−C bond lengths of 1.407(8) to 1.438(8) Å. The deviations in the Ti−C distances indicate that the titanium atom is bonded somewhat more strongly to C(1), C(2) and C(5) atoms with average distances of 2.34 Å than to C(3) and C(4) atoms (2.37 Å), but the cyclopentadienyl fragment can be still regarded as η^5-coordinated. A different situation has been observed for the [$Ph_2PCpTiCl_3$] complex[47] in which the distance between the titanium atom and the phosphorus-substituted carbon atom is slightly elongated in comparison to the other carbon atoms of the cyclopentadienyl ligand. The bond angle C(1)−P(1)−C(10) at the phosphorus atom of 100.3(2)° is smaller than N(1)−P(1)−C(1) of 108.6(2)° and N(1)−P(1)−C(10) 110.4(2)°. This phenomenon may be attributed to a higher steric demand of a shorter bound nitrogen substituent at the phosphorus atom [1.691(4) Å], while the electronegative character of the Et_2N group should work in an absolutely opposite direction. This leads to a greater contribution of the 3p orbital of the phosphorus atom to the P−N bond and as a consequence more 3s character in the P−C bond according to the well-known "rehybridisation" effect, also referred to as Bent's rule.[48] Introduction of an electronegative substituent X (e.g. NR_2) in a compound X−EY_n (e.g. $R_2N-PR'_2$) develops more p-orbital character of the E−X (e.g. P−N) bond, leaving more s character for the bonds E−Y (e.g. P−C), thus shortening them and enhancing Y−E−Y angles. The Ti−Cl distances as well as Cl−Ti−Cl angles have values typical of other related cyclopentadienyltitanium trichlorides.[49−51] Although the Et_2N group is oriented towards the metal centre, the Ti(1)−N(1) distance of 4.03 Å is considerably longer than the sum of the van der Waals radii of 3.82 Å.[52]

When [tBuCp−PtBu(Cl)] (**6**) is treated with $TiCl_4$ in hexane at a low temperature in the presence of Et_3N [{tBuCp−PtBu(Cl)}$TiCl_3$] (**39**) is obtained in almost quantitative yield as estimated by ^1H and ^{31}P NMR spectroscopy(Scheme 10). Complex **39** is, however, very soluble in aliphatic solvents so that an analytically pure sample could be isolated with 40% yield.



Scheme 10

Attempts to extend this synthetic strategy to other derivatives [$R_nCp-PtBu(Cl)$] (**1**−**3** and **5**) and [{$R_nCp-PtBu(Cl)$}$_2Z$] (**7**−**10**) failed. Only the sterically less encumbered [{$Cp-PtBu(Cl)$}$_2CMe_2$] (**11**) was successfully transformed into target complexes by the reaction with 1 and 2 equiv. of $TiCl_4$ to form complex isomeric mixtures of corresponding homobimetalic [{$(Cp-PtBu(Cl)]_2$-CMe_2}{$TiCl_3$}$_2$] (**40**) and *ansa*-[{$(Cp-PtBu(Cl)]_2$-CMe_2}$TiCl_2$] (**41**) compounds (Scheme 11).

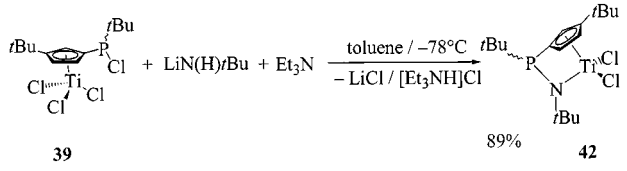


Scheme 11

According to ^1H and ^{31}P NMR spectroscopic data both complexes are formed in a high (ca. 90%) yield. The physical properties of **40** and **41** are totally different. **40** is only soluble in polar solvents, e.g. toluene, CH_2Cl_2, THF, and insoluble in aliphatic solvents, whereas the *ansa* complex **41** is practically unlimitedly soluble in aliphatic solvents. All of our efforts to purify these compounds by standard methods such as sublimation, liquid chromatography or recrystallisation have failed so far.

The fact that only sterically less demanding and more CH-acidic alkyl(chloro)cyclopentadienylphosphanes react with $TiCl_4$ in the presence of Et_3N to give complexes similar to **39** leads us to the hypothesis that in the mechanism of the reaction the key-step should be controlled by the acidity of the Cp protons. An analogous methodology has been used for the synthesis of [{Cp(CH$_2$)$_2$NR$_2$}TiCl$_3$] complexes by direct reaction of Cp ligand precursors and $TiCl_4$ in the presence of Et_3N as a base.[53,54]

The complex [{*t*BuCp−P*t*Bu(Cl)}TiCl$_3$] (**39**) is structurally related to [{R$_n$CpSiMe$_2$(Cl)}TiCl$_3$] derivatives bearing a reactive chlorine atom at the dimethylsilyl group that were then transformed into [{R$_n$CpSiMe$_2$(N*t*Bu)}TiCl$_2$] CGC-type of complexes.[55−58] Awarding all of our previous unsuccessful attempts to access this class of compounds with a phosphorus bridging group, the transformation of **39** (half-sandwich) into complex **42** of CGC-type proceeded in good yield (Scheme 12).



39 **42**

Scheme 12

The complex **42** is formed as a mixture of two diastereomers with respect to *syn* and *anti* orientation of the *t*Bu groups at the phosphorus atom and Cp ligand. Compound **42** was characterised by ^1H, ^{13}C, ^{31}P NMR spectroscopy and C,H,N elemental analyses.

Polymerisation of Ethylene

The preparative organotitanium chemistry described in the preceding sections was undertaken in part to provide precursors for an investigation of the catalytic polymerisation of ethylene in the presence of methylalumoxane (MAO), being suitable to roughly estimate the primary catalytic properties of the complexes.

Complexes **39** and **42** show moderate activities in the ethylene polymerisation at 20 and 80 °C (800 for **39** and 100 kg PE·mol^{-1}[Ti]·h^{-1}·bar^{-1} for **42**, MAO/[Ti] = 2000, T = 80 °C, p = 3 bar), while MAO-activated compounds **36**−**38** produce polyethylene with performances lower than 20 kg PE·mol^{-1}[M]·h^{-1}·bar^{-1} under the same polymerisation conditions. Related complexes [CpTiCl$_3$] (60), [Cp*TiCl$_3$] (600), [{Me$_4$CpCH$_2$CH$_2$NMe$_2$}TiCl$_3$] (200)[59] and [{Me$_4$CpSiMe$_2$N(*t*Bu)}TiCl$_2$] (950 kg PE·mol^{-1}·[Ti]·h^{-1}·bar^{-1})[60] show comparable and, under our experimental conditions, reproducible activities. The product is in all cases a highly linear polyethylene of high molecular weight ($10^5 < M_w < 1.4 \cdot 10^6$, determined viscosimetrically) having a melting point (DSC) in the range from 123 to 132 °C. Our main objective, however, was to compare the polymerisation activity of various organotitanium compounds and we have not investigated the morphology and the molecular weight distribution in detail. An investigation of the influence of the aminophosphanyl group attached to the cyclopentadienyl ligand on the catalytic behaviours of the complexes and the polymer properties is underway.

Conclusion

We have developed a new facile route to a class of P−N-functionalised phosphorylated cyclopentadienes, indenes and fluorenes **12**−**22**. Many attempts to obtain complexes **12**−**22** with group-4 transition metals Ti^{IV} and Zr^{IV} using classical procedures were, however, unsuccessful. We believe that the limiting factor is the high Lewis acidity of the Ti^{IV} and Zr^{IV} halides when they are treated with lithium and potassium salts of the ligand precursors giving complex mixtures of products. On the other hand, less Lewis-acidic Ti^{IV} and Zr^{IV} derivatives, e.g. Ti(NMe$_2$)$_4$, Zr(NMe$_2$)$_4$, do not react with the cyclopentadienylphosphanes under mild conditions due to a low CH acidity of these cyclopentadienes, while in the case of Ti(CH$_2$Ph)$_4$ or Zr(CH$_2$Ph)$_4$, again mixtures of products difficult to separate were formed at elevated temperatures. Several complexes could be synthesised only when trimethyltin-substituted amino(cyclopentadienyl)phosphane derivatives **31** and **32** were used as cyclopentadienylating agents. Surprising results have been obtained in the reaction of [*t*BuCp−P*t*Bu(Cl)] (**6**) with $TiCl_4$ in the presence of Et_3N at low temperature; the half-sandwich complex [{*t*BuCp−P*t*Bu(Cl)}TiCl$_3$] (**39**) was formed in a high yield. Compound **39** could be transformed into a CGC complex [{*t*BuCp−P*t*Bu(N*t*Bu)}TiCl$_2$] (**42**) by treatment with LiN(H)*t*Bu/Et_3N mixture in toluene. The isolated half-sandwich complexes [{R$_n$Cp−P*t*Bu(NEt$_2$)}TiCl$_3$] (**36**−**39** and **42**) were tested in the polymerisation of ethylene, some of them having activities comparable to known systems.[59][60]

Experimental Section

General Remarks: All manipulations involving air- and moisture-sensitive materials were carried out by standard Schlenk techniques under dry argon. Solvents were dried and distilled prior to use and stored under an inert gas. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C with Bruker AC250P, Bruker ARX300 and Varian VXR-400 spectrometers. Mass spectra (EI-MS) were recorded with a Varian CH-7a device using electron impact with an ionisation energy of 70 eV; all assignments were made with reference to the most abundant isotopes. C,H,N elemental analyses were carried out by the Microanalytical Division of Philipps-Universität Marburg. IR spectra were recorded with a Nicolet 510 FT-IR spectro-

meter. $[Cp_2CMe_2]$,[61] $[Ind_2CEt_2]$,[62] $[Ind_2(CH_2)_2]$ and $[IndCMe_2Cp]$,[63] $MesPCl_2$ (Mes = 2,4,6-$Me_3C_6H_2$) and $tBuPCl_2$,[64] Me_6IndH,[65] were prepared according to literature methods. Li salts of the cyclopentadienyl ligand precursors, indene and fluorene were obtained by deprotonation with a 1.6 M solution of *n*BuLi (purchased from Merck); $PhCH_2K$,[66] Ph_2CHK[67] by a standard procedure. MAO was used as 10% solution in toluene as received from Witco GmbH.

General Procedure for the Preparation of [$R_nCp-PR(Cl)$] (1−11): The total amount of dichlorophosphane ($RPCl_2$) (1 mol-equiv.; R = Alk or Ar) was added at once to a suspension of [R_nCp]Li (R_nCp = *t*BuCp, Me_4Cp, Ind, Flu) in hexane [in the case of bis(cyclopentadienyl) or bis(indenyl) diethyl ether had to be used] at −30 °C and the reaction mixture was stirred for 8 h, after warming to room temperature (1 h). Then the precipitated LiCl was removed by filtration. The filtrate was concentrated under vacuum (3 mbar) at room temperature to yield a product of an oily yellow liquid. Yield: 66−98%.

General Procedure for the Preparation of [$R_nCp-PR(NR^1R^2)$] (12−22): The total amount of HNR^1R^2 (2 mol) was immediately added to a solution of [$R_nCp-PR(Cl)$] (**1**−**6**) (1 mol) in diethyl ether at −20 °C and the reaction mixture was stirred for an additional 5 h at room temperature. Then the precipitated ammonium salt was removed by filtration. The filtrate was concentrated under vacuum at room temperature to yield a product of an oily yellow or red-yellow liquid. The yield, in all cases, was nearly quantitative.

General Procedure for the Preparation of [$R_nCp-PR(NR^1R^2)$]K (25−29): A solution of Ph_2CHK/$PhCH_2K$ (1 mol) was added slowly at −78 °C to a solution of [$R_nCp-PR(NR^1R^2)$] (**12**, **17**, **20** and **21**) (1 mol) in THF. The reaction mixture was stirred for 8 h, while warming to room temperature. The reaction mixture had a red colour except for the monoindenyl ligand derivatives that were green. Then the solvent was removed by evaporation under vacuum to give an oil. The oil solidified in pentane after several minutes to 2 d. Solvent-free potassium salts were isolated by filtration, washed twice with pentane and dried under vacuum. The yields, in all cases, were nearly quantitative.

General Procedure for the Preparation of [(Me_3Sn)-$R_nCp-PR(NR^1R^2)$] (31−34): A solution of Me_3SnCl (1 mol) in diethyl ether was added dropwise at −30 °C to a suspension of potassium salt [$R_nCp-PR(NR^1R^2)$]K (**25**−**28**) (1 mol) in diethyl ether. The reaction mixture was stirred for 8 h, while warming to room temperature. Then the precipitated KCl was removed by filtration. The filtrate was concentrated under vacuum at room temperature to yield a product of a white or pale yellow oil. The yield, in all cases, was nearly quantitative.

[Ind−P*t*Bu(Cl)] (1): Obtained from IndLi (3.54 g, 29.0 mmol) and $tBuPCl_2$ (4.77 g, 30.0 mmol). Isolated 4.61 g (19.3 mmol), yield 66%. *Isomer 1: tert*-Butylchloro(1*H*-inden-1-yl)phosphane (60%). ^1H NMR (300 MHz, [D_6]benzene): δ = 0.89 (d, 9 H, *t*Bu, $^3J_{HP}$ = 12.6 Hz), 3.99 (m, 1 H, Ind), 6.31−6.28 (dt, 1 H, Ind, $^3J_{H,H}$ = 4.2, $^3J_{HP}$ = 2.1 Hz), 6.66−6.64 (dt, 1 H, Ind, $^3J_{H,H}$ = 4.2 Hz), 7.13−7.01 (m, 2 H, Ind), 7.20−7.18 (d, 1 H, Ind), 7.81−7.78 (d, 1 H, Ind). $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): δ = 132.0. *Isomer 2: tert*-Butylchloro(1*H*-inden-2-yl)phosphane (25%). ^1H NMR (300 MHz, [D_6]benzene): δ = 0.98 (d, $^3J_{HP}$ = 13.3 Hz, 9 H, *t*Bu), 3.62 (dt, 1 H, Ind), 6.42−6.38 (m, 1 H, Ind), 6.72−6.68 (m, $^3J_{H,H}$ = 8.1, $^3J_{HP}$ = 1.9 Hz, 1 H, Ind), 7.18−7.00 (m, 3 H, Ind), 7.59−7.57 (m, 1 H, Ind). *Isomers 1 and 2:* $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene): δ = 26.7 (d, $^2J_{C,P}$ = 9 Hz, CH_3, *t*BuP), 26.8 (d, $^2J_{C,P}$ = 9.3 Hz, CH_3, *t*BuP), 34.5 (d, $^1J_{C,P}$ = 35.9 Hz, C, *t*BuP), 35.3 (d, $^1J_{C,P}$ = 38.1 Hz, C, *t*BuP), 51.4 (d, $^1J_{C,P}$ = 47.2 Hz, CH, Ind), 54.8 (d, $^1J_{C,P}$ = 44.3 Hz, CH, Ind), 121.8 (CH, Ind), 121.9 (CH, Ind), 124.4 (d, $J_{C,P}$ = 9 Hz, CH, Ind), 125.2, 125.3, 125.4, 127.3, 127.4 (CH, Ind), 132.5 (d, $J_{C,P}$ = 5.2 Hz, CH, Ind), 132.8 (d, $J_{C,P}$ = 2.2 Hz, CH, Ind), 133.5 (d, $J_{C,P}$ = 3.7 Hz, CH, Ind), 133.6 (d, $J_{C,P}$ = 3.2 Hz, CH, Ind), 143.7 (d, $J_{C,P}$ = 11.3 Hz, C, Ind), 144.4 (d, $J_{C,P}$ = 22.5 Hz, C, Ind). $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): δ = 127.2. *Isomer 3: tert*-Butylchloro(1*H*-inden-3-yl)phosphane (15%). ^1H NMR (300 MHz, [D_6]benzene): δ = 1.08 (d, $^3J_{HP}$ = 17.9 Hz, 9 H, *t*Bu), 3.00 (d, $^3J_{H,H}$ = 2 Hz, 2 H, Ind), 7.70−7.64 (m, 1 H, Ind), 6.79 (dt, $^3J_{H,H}$ = 2, $^3J_{HP}$ = 4.1 Hz, 1 H, Ind), 7.28−7.15 (m, 3 H, Ind). $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene): δ = 26.3 (d, $^2J_{C,P}$ = 18.1 Hz, CH_3), 35.3 (d, $^1J_{C,P}$ = 27.8 Hz, C, *t*Bu), 39.9 (CH, Ind), 122.3 (d, $J_{C,P}$ = 6 Hz, CH, Ind), 124.2, 125.4, 126.5 (CH, Ind), 141.0 (d, $^1J_{C,P}$ = 46.5 Hz, C, Ind), 144.2 (d, $^2J_{C,P}$ = 12.1 Hz, CH, Ind), 144.4 (d, $J_{C,P}$ = 3.7 Hz, C, Ind), 145.8 (d, $J_{C,P}$ = 21.3 Hz, C, Ind). $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): δ = 102.4. EI-MS: *m*/*z* (%) = 238 (8) [M^+], 182 (9) [M^+ − *t*Bu], 115 (26) [Ind], 57 (100) [*t*Bu]. $C_{13}H_{16}PCl$ (238.70): calcd. C 65.41, H 6.76; found C 65.02, H 6.37.

[Flu−P*t*Bu(Cl)] (2):[40] Obtained from FluLi (2.61 g, 15.2 mmol) and $tBuPCl_2$ (2.41 g, 15.2 mmol). Isolated 4.13 g (14.3 mmol), yield 94%. ^1H NMR (300 MHz, [D_6]benzene): δ = 0.41 (d, $^3J_{HP}$ = 12.9 Hz, 9 H, *t*Bu), 7.98−7.90 (m, 1 H, Flu), 4.41 (s, 1 H, Flu), 7.18−6.95 (m, 4 H, Flu), 7.45−7.40 (m, 3 H, Flu). $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene): δ = 26.8 (d, $^2J_{C,P}$ = 16.7 Hz, CH_3, *t*BuP), 36.3 (d, $^1J_{C,P}$ = 40.7 Hz, C, *t*BuP), 51.2 (d, $^1J_{C,P}$ = 49.4 Hz, CH, Flu), 120.4, 120.5, 125.9, 126.1, 126.7, 126.8, 127.3, 127.8 (CH, Flu), 141.2 (d, $J_{C,P}$ = 15 Hz, C, Flu), 141.3 (C, Flu), 142.4 (d, $J_{C,P}$ = 15 Hz, C, Flu), 144.1 (C, Flu). $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): δ = 132.0. EI-MS: *m*/*z* (%) = 288 (3) [M^+], 231 (1) [M^+ − *t*Bu], 165 (100) [Flu]. $C_{17}H_{18}ClP$ (288.76): calcd. C 70.71, H 6.28; found C 70.14, H 6.40.

[Ind−PMes(Cl)] (3): Obtained from IndLi (2.5 g, 20.5 mmol) and $MesPCl_2$ (4.53 g, 20.5 mmol). Isolated 5.07 g (16.9 mmol), yield 82%. *Mixture of Isomers:* ^1H NMR (300 MHz, [D_6]benzene): δ = 2.5−1.8 (several s and d, 9 H, CH_3), 5.3−4.5 (several m, 1 H, Ind), 7.5−6.2 (several m, 7 H, Ind and Mes). $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene): δ = 25.0−21.0 (10 resonances, CH_3), 56.0−39.0 (3 d, Ind), 126.0−120.0 (22 resonances, CH, Ind/Mes), 127.7 (CH, Ind/Mes), 131.0−129.0 (6 d, CH, Ind/Mes), 132.0 (3 d, C, Ind/Mes), 132.5 (2 d, C, Ind/Mes), 134 (d, C, Ind/Mes), 137.0−136.0 (2 d and 1 s, C, Ind/Mes), 142.0−141.0 (3 s, C, Ind/Mes), 145.0−144.5 (3 d, C, Ind/Mes). $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): δ = 70.7, 83.5, 84.3. EI-MS: *m*/*z* (%) = 300 (25) [M^+], 265 (10), [M^+ − Cl], 185 (100), [M^+ − Ind], 119 (42) [Mes], 115 (56) [Ind]. $C_{18}H_{18}ClP$ (300.77): calcd. C 71.88, H 6.03; found C 71.21, H 5.87.

[Me_6C_9H−P*t*Bu(Cl)] (4): Obtained from [Me_6C_9H]Li (3.0 g, 14.5 mmol) and $tBuPCl_2$ (2.32 g, 14.5 mmol). Isolated 3.98 g (12.3 mmol), yield 85%. ^1H NMR (300 MHz, [D_6]benzene): δ = 0.81 (d, $^3J_{HP}$ = 12.9 Hz, 9 H, *t*Bu), 2.04 (s, 3 H, CH_3), 2.06 (s, 6 H, 2 CH_3), 2.20 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.45 (d, $^4J_{HP}$ = 2 Hz, 3 H, CH_3), 4.14 (s, 1 H, Me_6C_9H). $^{13}C\{^1H\}$ NMR (75 MHz, [D_6]benzene): δ = 15.1, 16.0 (CH_3), 16.2 (d, $^3J_{C,P}$ = 7.5 Hz, CH_3, Me_6C_9H), 16.3 (CH_3, Me_6C_9H), 18.9 (d, $^4J_{C,P}$ = 19.6 Hz, CH_3, Me_6C_9H), 24.5 (CH_3, Me_6C_9H), 26.6 (d, $^2J_{C,P}$ = 17.3 Hz, CH_3, *t*BuP), 36.2 (d, $^1J_{C,P}$ = 40.8 Hz, C, *t*BuP), 57.7 (d, $^1J_{C,P}$ = 52.1 Hz, C, Me_6C_9H), 126.7, 129.3, 131.4, 134.7, 135.2 (C, Me_6C_9H), 138.1 (d, $J_{C,P}$ = 8.5 Hz, C, Me_6C_9H), 140.0, 141.7 (C, Me_6C_9H). $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]benzene): δ = 45.3. EI-MS: *m*/*z* (%) = 322

(3) [M^+], 199 (100) [Me_6C_9H]. $C_{19}H_{28}ClP$ (322.86): calcd. C 70.68, H 8.74; found C 70.05, H 8.49.

[Me_4C_5H-P*t*Bu(Cl)] (5): Obtained from [Me_4C_5H]Li (1.85 g, 14.5 mmol) and of *t*BuPCl_2 (2.76 g, 14.5 mmol). Isolated 2.49 g (10.6 mmol), yield 73%. *Isomer 1: tert*-butylchloro(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)phosphane. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 0.92 (d, $^3J_{HP}$ = 13.1 Hz, 9 H, *t*BuP), 1.50 (s, 3 H, CH_3, Me_4C_5H), 1.52 (s, 3 H, CH_3, Me_4C_5H), 1.85 (s, 3 H, CH_3, Me_4C_5H), 2.01 (s, 3 H, CH_3, Me_4C_5H), 3.28 (d, $^2J_{HP}$ = 6.8 Hz, 1 H, Me_4C_5H). *Isomer 2: tert*-Butylchloro(1,2,4,5-tetramethylcyclopenta-2,4-dien-3-yl)phosphane. 1.05 (d, $^3J_{HP}$ = 13.9 Hz, 9 H, *t*BuP), 1.26 (d, 3 H, CH_3), 1.44 (m, 3 H, CH_3), 1.56 (d, 3 H, CH_3), 1.98 (d, 3 H, CH_3), 3.06 (m, 1 H, Me_4C_5H). *Both Isomers:* ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene): δ = 11.1, 11.3, 12.0, 13.9, 14.2, 15.2, 16.9 (CH_3), 26.7 (d, $^2J_{C,P}$ = 18.8 Hz, CH_3, *t*Bu, *isomer 2*), 27.0 (d, $^2J_{C,P}$ = 17.5 Hz CH_3, *t*Bu, *isomer 1*), 35.2 (d, $^1J_{C,P}$ = 37 Hz, C, *t*Bu, *isomer 2*), 36.4 (d, $^1J_{C,P}$ = 39.8 Hz, C, *t*Bu, *isomer 1*), 54.7 (CH, Me_4C_5H, *isomer 2*), 61.7 (d, $^1J_{C,P}$ = 49.2 Hz, CH, *isomer 1*, Me_4C_5H), 131.2, 134.1, 136.5, 137.6 150.1 (C, Me_4C_5H). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 34.5 (*isomer 2*; ca. 40%), 98.2 (*isomer 1*; ca. 60%). EI-MS: *m*/*z* (%) = 244 (12) [M^+], 187 (100) [M^+ − *t*Bu], 120 (65) [C_5Me_4]. $C_{13}H_{22}PCl$ (244): calcd. C 63.80, H 9.21; found C 63.41, H 9.22.

[*t*BuC_5H_4−P*t*Bu(Cl)] (6): Obtained from *t*BuCpLi (1.0 g, 7.81 mmol) and of *t*BuPCl_2 in hexane (9.6 mL, 7.81 mmol/0.81 M). Isolated 1.81 g (7.41 mmol), yield 95%. *Mixture of Isomers:* ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.2−1.0 (several d, 18 H, *t*Bu and *t*BuP), 3.25 (s, 1 H, *t*BuC_5H_4), 6.2 (several m, 1 H, *t*BuC_5H_4), 6.9 (several m, 1 H, *t*BuC_5H_4), 7.05 (several m, 1 H, *t*BuC_5H_4). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene): δ = 12.1 (CH_3, *t*BuC_5H_4), 26.1−30.0 (several d, CH_3, *t*BuP), 32.1 (m, C, *t*Bu), 34.2 (m, C, *t*BuP), 43.9, 124.8, 144.9 (m, CH, *t*BuC_5H_4), 157.0 (d, C, *t*BuC_5H_4), 159.9 (m, CH, *t*BuC_5H_4). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 103.0, 106.9, 107.2. EI-MS: *m*/*z* (%) = 229 (24) [M^+ − CH_3], 211 (57) [M^+ − Et], 155 (19) [*t*Bu$C_5H_4PH_2$], 107 (37) [*t*BuC_5H_4 − Me], 57 (100) [*t*Bu], 35 (53) [Cl]. $C_{13}H_{22}ClP$ (244.74): calcd. C 63.80, H 9.06; found C 63.39, H 8.72.

[{Ind−P*t*Bu(Cl)}$_2$(CH_2)$_2$] (7): Obtained from [Ind(CH_2)$_2$Ind]Li_2 (2.0 g, 7.04 mmol) and *t*BuPCl_2 (18.1 mL, 14.08 mmol/0.81 M). Isolated 2.47 g (4.79 mmol), yield 64%. *Mixture of Isomers:* ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 0.9−1.1 (4 d, 18 H, *t*BuP), 2.75 and 2.85 (2 s, 4 H, −$CH_2$$CH_2$−), 4.1 (several m, 2 H, Ind), 6.1−6.4 (several m, 1 H, Ind), 7.64−7.7 (several m, 8 H, Ind), 7.99−7.91 (several m, 1 H, Ind). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene): δ = 26.4−26.8 (CH_3, *t*BuP), 34.7−35.4 (−$CH_2$$CH_2$−), 50.0−50.5 (C, *t*BuP), 53.0−53.5, 119.7−119.8, 125.5−126.7, 127.2−127.3 (several resonances, CH, Ind), 144.6−145.1, 145.1, 145.8−146.2 (several resonances, C, Ind). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 127.7, 128.8, 128.9, 130.7, 131.3, 131.1, 131.3. EI-MS: *m*/*z* (%) = 253 (42) [MeInd(*t*Bu)P(Cl)H], 128 (100) [MeInd], 115 (38) [Ind], 57 (76) [*t*Bu]. $C_{28}H_{34}Cl_2P_2$ (502.15): calcd. C 66.80, H 6.81; found C 66.37, H 6.51.

[{Ind−P*t*Bu(Cl)}$_2$$CMe_2$] (8): Obtained from [(Ind)$_2$$CMe_2$]$Li_2$ (7.95 g, 18.44 mmol) and *t*BuPCl_2 (37.9 mL, 36.88 mmol/0.97 M). Isolated 9.43 g, yield > 95%. *Mixture of Isomers:* ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.0−1.5 (4 d, 18 H, *t*BuP), 1.8 (s, 6 H, CMe_2), 3.9−4.2 (m, 2 H, Ind), 6.6 (several m, 2 H, Ind), 7.1 (m, 4 H, Ind), 7.2−7.6 (several m, 2 H, Ind), 7.7 (m, 2 H, Ind). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 24.6 (CH_3, CMe_2), 25.7−26.8 (several resonances, CH_3, *t*BuP), 38.3−38.4 (several resonances, C, *C*Me_2), 48.5−48.8 (C, *t*BuP), 52.1−52.4, 121.8−122.4, 123.8−125.3, 125.4−127.0 (several resonances, CH, Ind), 143.0−144.9 (several resonances, C, Ind). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 130.1, 130.2, 130.3, 131.0, 131.2, 131.3, 131.4. $C_{29}H_{36}Cl_2P_2$ (516.16): calcd. C 67.31, H 7.01; found C 67.13, H 6.89.

[{Ind−P*t*Bu(Cl)}$_2$$CEt_2$] (9): Obtained from [(Ind)$_2$$CEt_2$]$Li_2$ (4.0 g, 12.85 mmol) and *t*BuPCl_2 (26.5 mL, 25.7 mmol/0.97 M). Isolated 6.48 g, yield 92%. *Mixture of Isomers:* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.75−0.85 (m, 3 H, −$CH_2$$CH_3$), 1.3−1.5 (3 d, 9 H, *t*BuP), 2.23−2.27 (m, 2 H, −$CH_2$$CH_3$), 4.29 (s, 1 H, Ind), 6.56 (s, 1 H, Ind), 7.0−7.2 (m, 2 H, Ind), 7.58 (d, $J_{H,H}$ = 7.3 Hz, 1 H, Ind), 7.84 (d, $J_{H,H}$ = 7.3 Hz, 1 H, Ind). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 129.4 (br. s), 130.8 (br. m) and 131.0. $C_{31}H_{40}Cl_2P_2$ (545.51): calcd. C 68.26, H 7.39; found C 67.93, H 7.01.

[{Ind−P*t*Bu(Cl)}CMe_2{Cp−P*t*Bu(Cl)}] (10): Obtained from [IndCMe$_2$Cp]Li_2 (3.86 g, 16.5 mmol) and *t*BuPCl_2 (34.0 mL, 33.0 mmol/0.97 M). Isolated 3.9 g (8.4 mmol), yield 50%. *Mixture of Isomers:* ^{1}H NMR (400 MHz, [D$_6$]benzene): the spectrum is not informative, very complex set of partially low-resolved signals. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 106.7 (3 signals), 106.8, 124.6, 131.1, 131.7. $C_{25}H_{34}Cl_2P_2$ (467.39): calcd. C 64.24, H 7.33; found C 64.01, H 7.52.

[{Cp−P*t*Bu(Cl)}$_2$$CMe_2$] (11): Obtained from [Cp$_2$$CMe_2$]$Li_2$ (5.0 g, 27.20 mmol) and *t*BuPCl_2 (56.0 mL, 54.4 mmol/0.97 M). Isolated 9.26 g (22.2 mmol), yield 80%. *Mixture of Isomers:* ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.9−1.45 (several d, 18 H, *t*BuP), 1.45 (m, 6 H, CMe_2), 3.0−3.3 (s and several m, 2 H, Cp), 6.2−6.4 (several m, 2 H, Cp), 6.6−6.95 (m, 4 H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 23.0−23.5 (2 resonances, CH_3, CMe_2), 25.5−26.3 (several resonances, CH_3, *t*BuP), 36.0−40.0 (several resonances, C, *C*Me_2), 43.5−46.0 (several resonances, C, *t*BuP), 51.0−55.0 (several resonances, CH, Cp), 129.0−133.0 (CH, Cp), 140.0−148.0 (several resonances, C, Cp). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 100.7, 101.0, 104.7, 104.8, 104.9, 105.0, 105.1 (2 signals), 105.2, 105.3, 105.4, 105.7, 105.8, 105.9, 106.0, 106.1. EI-MS: *m*/*z* (%) = 416 (1) [M^+], 187 (76) [Cp(*t*Bu)PCl], 172 (92) [Cp$_2$$CMe_2$], 170 (92) [$M^+$ − 2 *t*BuPCl], 57 (100) [*t*Bu]. $C_{21}H_{32}Cl_2P_2$ (416.13): calcd. C 60.44, H 7.73; found C 60.63, H 7.56.

[Ind−P*t*Bu(NEt_2)] (12): Obtained from [Ind−P*t*Bu(Cl)] (**1**) (2.39 g, 10.0 mmol) and Et_2NH (3.1 mL, > 20 mmol). Isolated 2.74 g (9.9 mmol), yield > 95%. IR (film): $\tilde{\nu}$ = 3000, 2950, 2875, 2864, 2396, 1558, 1457, 1180, 1093, 874, 773, 736 (P−N), 415 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 0.83 (t, $^3J_{H,H}$ = 5.4 Hz, 6 H, −NCH_2CH_3), 1.19 (d, $^3J_{HP}$ = 12.9 Hz, 9 H, *t*Bu), 2.93 (m, 4 H, −NCH_2CH_3), 3.0−3.1 (m, 2 H, Ind), 6.43 (m, 1 H, Ind), 7.12 (m, 2 H, Ind), 7.18−7.23 (m, 1 H, Ind), 7.80 (m, 1 H, Ind). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene): δ = 15.1 (d, $^3J_{C,P}$ = 3.2 Hz, −NCH_2CH_3), 28.1 (d, $^2J_{C,P}$ = 16.1 Hz, CH_3, *t*Bu), 33.65 (d, $^1J_{C,P}$ = 17.6 Hz, C, *t*Bu), 40.2 (CH, Ind), 46.5 (d, $^2J_{C,P}$ = 15.7 Hz, −NCH_2CH_3), 121.0 (d, $^3J_{C,P}$ = 7.4 Hz, CH, Ind), 123.6, 124.9, 126.4, 136.6 (CH, Ind), 142.3 (d, $^1J_{C,P}$ = 25.5 Hz, C, Ind), 143.4 (C, Ind), 148.0 (d, $^2J_{C,P}$ = 23.6 Hz, C, Ind). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 63.9. EI-MS: *m*/*z* (%) = 275 (7) [M^+], 218 (76) [M^+ − *t*Bu]. $C_{17}H_{28}NP$ (277.38): calcd. C 73.61, H 10.17, N 5.05; found C 73.32, H 9.74, N 4.91.

[Ind−P*t*Bu(NH*t*Bu)] (13): Obtained from [Ind−P*t*Bu(Cl)] (**1**) (2.39 g, 10 mmol) and *t*BuNH_2 (3.2 mL, > 20 mmol). Isolated 2.7 g (9.8 mmol), yield > 95%. IR (film): $\tilde{\nu}$ = 3000, 2961, 2771, 2380, 1635, 1578, 1540, 1192, 1180, 953, 736 (P−N), 656 cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 1.05 (d, $^3J_{HP}$ = 12.8 Hz, 9 H, *t*BuP), 1.15 (s, 9 H, *t*BuN), 1.68 (d, $^2J_{HP}$ = 11.9 Hz, 1 H, −NH), 3.07 (m,

2 H, Ind), 6.22 (m, 1 H, Ind), 7.12−7.18 (dt, 2 H, Ind), 7.24 (d, 1 H, Ind), 7.80 (d, 1 H, Ind). $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene): δ = 26.6 (d, $^2J_{C,P}$ = 15 Hz, CH_3, *t*BuP), 27.4 (d, $^1J_{C,P}$ = 16.4 Hz, CH_3, *t*BuP), 32.1 (d, $^3J_{C,P}$ = 8.3 Hz, C, *t*BuN), 39.4 (d, $^3J_{C,P}$ = 2.8 Hz, CH, Ind), 50.7 (d, $^2J_{C,P}$ = 17.2 Hz, C, *t*BuN), 122.4 (d, $^3J_{C,P}$ = 6.2 Hz, CH, Ind), 123.8, 125.0, 126.3, 141.1 (CH, Ind), 144.6 (C, Ind), 147.4 (d, $J_{C,P}$ = 32.4 Hz, C, Ind), 147.7 (d, $J_{C,P}$ = 23.6 Hz, C, Ind). $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]benzene): δ = 21.7. EI-MS: *m*/*z* (%) = 275 (9) [M$^+$], 218 (65) [M$^+$ − *t*Bu], 162 (100) [M − 2 *t*Bu]. $C_{17}H_{28}NP$ (277.38): calcd. C 73.61, H 10.17, N 5.05; found C 73.19, H 9.77, N 4.89.

[Ind−P*t*Bu(NHPh)] (14): Obtained from [Ind−P*t*Bu(Cl)] (**1**) (2.9 g, 12.14 mmol) and $PhNH_2$. (2.2 mL, 24.28 mmol). Isolated 3.47 g (11.77 mmol), yield > 95%. ^1H NMR (200 MHz, [D$_6$]benzene): δ = 1.02 (d, $^3J_{HP}$ = 15.8 Hz, 9 H, *t*BuP), 1.33 (d, $^2J_{HP}$ = 13 Hz, 1 H, −NH), 3.01 (m, 2 H, Ind), 6.26 (m, 1 H, Ph and Ind), 6.76−7.24 (several m, 8 H, Ph and Ind), 7.97 (d, 1 H, Ind). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D$_6$]benzene): δ = 25.0 (d, $^2J_{C,P}$ = 15.5 Hz, CH_3, *t*BuP), 31.0 (d, C, *t*BuP), 38.3 (d, $^3J_{C,P}$ =3 Hz, CH, Ind), 113.6, 115.4, 118.0, 122.5, 123.6, 123.7, 125.0, 128.1, 128.8 (CH, Ph/Ind), 137.1 (d, $^2J_{C,P}$ = 2.5 Hz, C, Ind), 140.0 (C, Ind), 143.0 (d, $^2J_{C,P}$ = 4.5 Hz, C, Ph), 145.2 (d, C, Ind), 146.5 (d, $J_{C,P}$ = 17.5 Hz, C, Ind). $^{31}P\{^1H\}$ NMR (81.0 MHz, [D$_6$]benzene): δ = 29.5. $C_{19}H_{24}NP$ (297.38): calcd. C 76.74, H 8.13, N 4.71; found C 76.10, H 8.25, N 4.63.

[Me$_6$C$_9$H−P*t*Bu(NH*t*Bu)] (15): Obtained from [Me$_6$C$_9$H−P*t*Bu(Cl)] (**4**) (3.44 g, 10.6 mmol) and *t*BuNH$_2$ (3.4 mL, >20 mmol). Isolated 2.85 g (7.94 mmol), yield 75%. ^1H NMR (200 MHz, [D$_6$]benzene): δ = 0.93 (d, $^3J_{HP}$ = 11.2 Hz, 9 H, *t*BuP), 1.31 (s, 9 H, *t*BuN), 1.98 (d, $^2J_{HP}$ = 2.5 Hz, 1 H, NH), 2.21 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.31 (s, 6 H, 2 CH_3), 2.57 (s, 3 H, CH_3), 2.80 (s, 3 H, CH_3), 3.85 (s, 1 H, Me$_6$C$_9$*H*). $^{13}C\{^1H\}$ NMR (50 MHz, [D$_6$]benzene): δ = 15.7, 16.5, 16.8, 19.4, 19.8, 26.0 (CH_3, Me$_6$C$_9$), 27.9 (d, $^2J_{C,P}$ = 16.1 Hz, CH_3, *t*BuP), 32.5 (d, $^3J_{C,P}$ = 7.8 Hz, CH_3, *t*BuN), 32.7 (d, CH, Me$_6$C$_9$H), 33.5 (d, $^1J_{C,P}$ = 16.9 Hz, C, *t*BuP), 51.3 (d, $^2J_{C,P}$ = 19.4 Hz, C, *t*BuN), 126.5, 133.5, 133.7, 140.8 (C, Me$_6$C$_9$H), 141.3 (d, $J_{C,P}$ = 6.9 Hz, C, Me$_6$C$_9$H). $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]benzene): δ = 51.0. EI-MS: *m*/*z* (%) = 359 (2) [M$^+$], 302 (16) [M$^+$ − *t*Bu], 199 (34) [Me$_6$C$_9$H]. $C_{23}H_{38}NP$ (359.54): calcd. C 76.84, H 10.65, N 3.90; found C 76.43, H 10.47, N 3.81.

[Ind−PMes(NH*t*Bu)] (16): Obtained from [Ind−PMes(Cl)] (**3**) (3.01 g, 10 mmol) and *t*BuNH$_2$ (3.1 mL, > 20 mmol). Yield > 95%. ^1H NMR (200 MHz, [D$_6$]benzene): δ = 1.32 (s, 9 H, *t*BuN), 2.15 (s, 3 H, CH_3), 2.45 (d, $^2J_{HP}$ = 11.6 Hz, 1 H, -NH), 2.64 (s, 6 H, 2 CH_3), 3.20 (m, 1 H, Ind), 6.34 (m, 1 H, Ind), 6.47 (m, 1 H, Ind), 6.80 (s, 2 H, Mes), 7.11−7.24 (m, 2 H, Ind and Mes), 7.31−7.35 (m, 1 H, Ind and Mes), 7.4−7.6 (m, 1 H, Ind and Mes). $^{13}C\{^1H\}$ NMR (50 MHz, [D$_6$]benzene): δ = 19.7 (CH_3, Mes), 21.0 (d, $^3J_{C,P}$ = 23.2 Hz, CH_3, Mes), 30.65 (d, $^3J_{C,P}$ = 9 Hz, C, *t*BuP), 38.0 (CH, Ind), 49.9 (d, $^2J_{C,P}$ = 21.3 Hz, C, *t*BuN), 120.4, 122.4, 123.5, 124.9 (CH, Ind/Mes), 128.8 (d, $^3J_{C,P}$ = 12.5 Hz, CH, Ind/Mes), 133.3 (d, $J_{C,P}$ = 24.5 Hz, C, Ind/Mes), 133.9 (d, $^3J_{C,P}$ = 9.5 Hz, CH, Ind/Mes), 141.7 (d, $^2J_{C,P}$ = 17.5 Hz, CH, Ind/Mes), 143.0 (d, $J_{C,P}$ = 6.1 Hz, C, Ind/Mes), 143.8 (d, $J_{C,P}$ = 5.3 Hz, C, Ind/Mes), 144.7 (d, $J_{C,P}$ = 13.1 Hz, C, Ind/Mes), 146.0 (d, $J_{C,P}$ = 7 Hz, C, Ind/Mes). $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]benzene): δ = 4.1. EI-MS: *m*/*z* (%) = 337 (1) [M$^+$], 265 (12) [M$^+$ − N(H)*t*Bu], 218 (34) [M$^+$ − Mes], 115 (100) [Ind]. $C_{22}H_{30}NP$ (339.46): calcd. C 77.84, H 8.91, N 4.13; found C 77.42, H 9.22, N 4.23.

[Flu−P*t*Bu(NEt$_2$)] (17):[31] Obtained from [Flu−P*t*Bu(Cl)] (**2**) (2.88 g, 10 mmol) and Et_2NH (1.0 mL, > 20 mmol). Isolated 3.20 g (9.8 mmol), yield 98%.

[Flu−P*t*Bu(NH*t*Bu)] (18): Obtained from 2.88 g (10 mmol) [Flu−P*t*Bu(Cl)] (**2**) and 1.0 mL (> 20 mmol) of *t*BuNH$_2$. Isolated 3.24 g (9.95 mmol), yield > 95%. ^1H NMR (200 MHz, [D$_6$]benzene): δ = 0.58 (s, 9 H, *t*BuN), 0.89 (d, $^3J_{HP}$ = 12.5 Hz, 9 H, *t*BuP), 1.56 (d, $^2J_{HP}$ = 10.3 Hz, 1 H, -NH), 3.84 (s, 1 H, Flu), 7.08−7.15 (m, 5 H, Flu), 7.23−7.27 (m, 1 H, Flu), 7.49−7.53 (m, 2 H, Flu). $^{13}C\{^1H\}$ NMR (50 MHz, [D$_6$]benzene): δ = 25.8 (d, $^2J_{C,P}$ = 16.5 Hz, CH_3, *t*BuP), 30.0 (d, $^1J_{C,P}$ = 13.6 Hz, C, *t*BuP), 30.4 (d, $^3J_{C,P}$ = 7.8 Hz, C, *t*BuN), 47.3 (d, $^1J_{C,P}$ = 39.2 Hz, C, Flu), 48.6 (d, $^2J_{C,P}$ = 18.2 Hz, C, *t*BuN), 118.5, 119.1, 124.1 (2 signals), 124.3, 124.9, 125.1, 125.7 (CH, Flu), 139.1 (d, $J_{C,P}$ = 3.3 Hz, C, Flu), 142.3, 140.8 (C, Flu), 147.0 (d, $J_{C,P}$ = 15.1 Hz, C, Flu). $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]benzene): δ = 49.5. EI-MS: *m*/*z* = 325 (1) [M$^+$], 268 (5) [M$^+$ − *t*Bu], 212 (12) [M$^+$ − 2 *t*Bu+H], 165 (36) [Flu]. $C_{21}H_{28}NP$ (325.43): calcd. C 77.51, H 8.67, N 4.31; found C 77.10, H 8.13, N 4.17.

[Me$_4$C$_5$H−P*t*Bu(NH*t*Bu)] (19): Obtained from [Me$_4$Cp−P*t*Bu(Cl)] (**5**) (2.44 g, 10 mmol) and *t*BuNH$_2$ (3.1 mL, > 20 mmol). Isolated 2.2 g (7.8 mmol), yield 78%. ^1H NMR (300 MHz, [D$_6$]benzene): δ = 0.94 (d, $^3J_{HP}$ = 12.4 Hz, 9 H, *t*BuP), 1.03 (s, 9 H, *t*BuN), 1.64 (s, 6 H, 2 CH_3), 1.98 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 2.11 (br. s., 1 H, −NH), 2.6 (m, 1 H, Me$_4$C$_5$H). $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]benzene): δ = 17.6 (CH_3), 27.2 (CH_3), 27.4 (d, $J_{C,P}$ = 3.8 Hz, CH_3), 27.7 (CH_3), 32.2 (d, $^3J_{C,P}$ = 6.2 Hz, C, *t*BuP), 54.2 (d, $^2J_{C,P}$ = 6.2 Hz, C, *t*BuN), 60.8 (d, $^1J_{C,P}$ = 36.9 Hz, CH, Me$_4$C$_5$H), 133.0, 136.6, 144.9 (C, Me$_4$C$_5$H), 152.3 (d, $J_{C,P}$ = 6.6 Hz, C, Me$_4$C$_5$H). $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]benzene): δ = 21.3. EI-MS: *m*/*z* (%) = 281 (7) [M$^+$], 224 (100) [M$^+$ − *t*Bu], 168 (22) [M$^+$ − 2 *t*Bu]. $C_{17}H_{32}NP$ (281.42): calcd. C 72.56, H 11.46, N 4.98; found C 72.64, H 11.13, N 5.12.

[Me$_4$C$_5$H−P*t*Bu(NEt$_2$)] (20): Obtained from [Me$_4$Cp−P*t*Bu(Cl)] (**5**) (2.44 g, 10 mmol) and Et_2NH (3.3 mL, > 20 mmol). Isolated 2.79 g (9.9 mmol), yield > 95%. *Mixture of Isomers:* IR (film): $\tilde{\nu}$ = 3000, 2858, 2733, 2361, 1629, 1579, 1547, 1195, 1157, 958, 723 (P−N), 680. ^1H NMR (200 MHz, [D$_6$]benzene): δ = 0.87 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, $-NCH_2CH_3$), 1.19 (d, $^3J_{HP}$ = 13.2 Hz, 9 H, *t*BuP), 1.80 (s, 3 H, CH_3, Me$_4$C$_5$H), 1.87 (s, 3 H, CH_3, Me$_4$C$_5$H), 2.10 (s, 3 H, CH_3, Me$_4$C$_5$H), 2.21 (s, 3 H, CH_3, Me$_4$C$_5$H), 2.8−3.0 (m, 5 H, $-NCH_2CH_3$ and Me$_4$C$_5$H). $^{13}C\{^1H\}$ NMR (50 MHz, [D$_6$]benzene): δ = 11.1 ($-NCH_2CH_3$), 28.8−29.8 (several d, $J_{C,P}$ = 7.8 Hz, CH_3), 34.8−35.5 ($-NCH_2CH_3$), 46.6−47.6 (3 d, $^2J_{C,P}$ = 20.2 Hz, C, *t*BuP), 53.1 (d, $^2J_{C,P}$ = 3.6 Hz, C, *t*BuN), 61.2, 61.9, 62.8 (CH, Me$_4$C$_5$H), 151.9−133.6 (several resonances, C, Me$_4$C$_5$H). $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]benzene): δ = 77.4, 86.4, 114.5. EI-MS: *m*/*z* (%) = 281 (2) [M$^+$], 224 (92) [M$^+$ − *t*Bu], 160 (38) [*t*BuPNEt$_2$], 153 (57) [Me$_4$C$_5$HP], 121 (19) [Me$_4$C$_5$H], 104 (100) [HPNEt$_2$], 72 (14) [NEt$_2$]. $C_{17}H_{32}NP$ (281.42): calcd. C 72.56, H 11.46, N 4.98; found C 72.17, H 11.33, N 5.10.

[*t*BuC$_5$H$_4$−P*t*Bu(NEt$_2$)] (21): Obtained from [*t*BuCp−P*t*Bu(Cl)] (**6**) (1.67 g, 10.51 mmol) and Et_2NH (2.5 mL, > 21 mmol). Yield > 95%. *Mixture of Isomers:* IR (film): $\tilde{\nu}$ = 3000, 2965, 1575, 1458, 1386, 922, 746 (P−N), 642 cm^{-1}. ^1H NMR (250 MHz, [D$_6$]benzene): δ = 0.9−1.3 (several m, 24 H, *t*Bu, *t*BuP and $-NCH_2CH_3$), 3.0 (m, 4 H, $-NCH_2CH_3$), 3.18 (s, 1 H, *t*BuC$_5$H$_4$), 6.1 (several m, 1 H, *t*BuC$_5$H$_4$), 6.35 (several m, 1 H, *t*BuC$_5$H$_4$), 6.6−6.75 (several m, 1 H, *t*BuC$_5$H$_4$). $^{13}C\{^1H\}$ NMR (50 MHz, [D$_6$]benzene): δ = 15.0 ($-NCH_2CH_3$), 28.8−28.9 (several d, CH_3, *t*BuP), 29.9, 31.0 ($-NCH_2CH_3$), 46.2−44.2 (several d, C, *t*BuN, *t*BuC$_5$H$_4$ and *t*BuP),

124.6, 124.7, 125.7 (CH, tBuC$_5$H$_4$), 133.7−162.7 (several resonances, CH, tBuC$_5$H$_4$). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 72.4, 74.9, 75.7. EI-MS: m/z (%) = 281 (3) [M$^+$], 224 (100) [M$^+$ − tBu], 160 (6) [tBuPNEt$_2$], 57 (68) [tBu]. C$_{17}$H$_{32}$NP (281.42): calcd. C 72.56, H 11.46, N 4.98; found C 72.34, H 11.01, N 5.32.

[tBuC$_5$H$_4$−PtBu(NHtBu)] (22): Obtained from [tBuCp−PtBu(Cl)] (**6**) (1.53 g, 6.26 mmol) and tBuNH$_2$ (2.0 mL, > 20 mmol). Yield > 95%. *Mixture of Isomers:* ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.16−1.31 (several m, 18 H, tBuN, tBuP), 2.9−3.20 (br. s, 1 H, tBuC$_5$H$_4$), 6.15−6.94 (several m, 3 H, tBuC$_5$H$_4$). ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = 26.3−26.8 (several d, CH$_3$), 41.0−44.1(d, C, tBuP, $^2J_{C,P}$ = 12.8 Hz), 50.77 (d, C, tBuN), 124.5, 124.7, 125.3 (CH, tBuC$_5$H$_4$), 133.9−162.2 (several resonances, CH, tBuC$_5$H$_4$). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 22.7, 26.1, 26.2. EI-MS: m/z (%) = 224 (100) [M$^+$ − tBu], 160 (4) [tBuPNH(tBu)]. C$_{17}$H$_{32}$PN (281.42): calcd. C 72.56, H 11.46, N 4.98; found C 72.61, H 11.21, N 5.13.

[Ind−PtBu(NtBu)]Li$_2$ (23): Obtained from [Ind−PtBu(NHtBu)] (**13**) (2.75 g, 10 mmol) and nBuLi (13.4 mL, 20 mmol/1.5 N). Isolated 3.26 g (9.7 mmol), yield 97%. ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 0.91 (d, $^3J_{HP}$ = 12.1 Hz, 9 H, tBuP), 1.01 (s, 9 H, tBuN), 5.87 (m, 1 H, Ind), 6.28−6.35 (m, 2 H, Ind), 6.58 (m, 1 H, Ind), 7.15 (m, 1 H, Ind), 8.01 (m, 1 H, Ind). ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF): δ = 26.9 (d, $^2J_{C,P}$ = 16.5 Hz, CH$_3$, tBuP), 32.0 (d, $^3J_{C,P}$ = 9.1 Hz, CH$_3$, tBuN), 35.6 (d, $^1J_{C,P}$ = 17.4 Hz, C, tBuP), 52.1 (d, $^2J_{C,P}$ = 16.5 Hz, C, tBuN), 91.2, 94.9, 112.7, 118.2, 119.4, 121.1 (CH, Ind); C (Ind) not observed.

[Flu−PtBu(NHtBu)]Li (24): Obtained from [Flu−PtBu(NHtBu)] (**18**) (0.35 g, 1.11 mmol) and nBuLi (0.75 mL, 1.12 mmol/1.5 N). Isolated 0.31 g (0.94 mmol), yield 85%. ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 0.90 (d, $^3J_{HP}$ = 12 Hz, 9 H, tBuP), 0.96 (s, 9 H, tBuN), 2.75 (d, $^2J_{HP}$ = 9.7 Hz, 1 H, −NH), 6.3 (t, 2 H, Flu), 6.7 (t, 2 H, Flu), 7.11−8.21 (br. m, 4 H, Flu). ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF): δ = 28.0 (d, $^2J_{C,P}$ = 16.5 Hz, CH$_3$, tBuP), 31.7 (d, $^3J_{C,P}$ = 9.8 Hz, tBuN), 34.4 (d, $^1J_{C,P}$ = 6.5 Hz, C, tBuP), 50.5 (d, $^2J_{C,P}$ = 18.1 Hz, C, tBuN), 108.9, 115.8, 117.4, 118.7, 119.3 (CH, Flu).

[Me$_4$C$_5$−PtBu(NEt$_2$)]K (25): Obtained from Ph$_2$CHK(THF) (4.26 g, 15.31 mmol) and [Me$_4$Cp−PtBu(NEt$_2$)] (**20**) (4.31 g, 15.31 mmol). The product was recrystallised from THF. Yield > 95%. ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 0.93 (t, $^3J_{H,H}$ = 7 Hz, 6 H, −NCH$_2$*CH$_3$*), 1.08 (d, $^3J_{HP}$ = 12 Hz, 9 H, tBuP), 1.94, 2.22 (s, 6 H, CH$_3$, Me$_4$C$_5$), 2.94 (m, 4 H, −N*CH$_2$*CH$_3$). ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF): δ = 11.9 (CH$_3$, Me$_4$C$_5$), 15.3 (d, $^3J_{C,P}$ = 7.2 Hz, CH$_3$, −NCH$_2$*CH$_3$*), 30.5 (d, $^2J_{C,P}$ = 18.6 Hz, CH$_3$, tBu), 33.5 (d, $^1J_{C,P}$ = 17.3 Hz, −N*CH$_2$*CH$_3$), 47.1 (d, $^2J_{C,P}$ = 17.8 Hz, C, tBuP), 108.3 (C, Me$_4$C$_5$), 112.3 (d, $J_{C,P}$ = 7.2 Hz, C, Me$_4$C$_5$), 128.9, 129.4 (C, Me$_4$C$_5$), 145.1 (d, $J_{C,P}$ = 19.7 Hz, C, Me$_4$C$_5$). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, 25 °C): δ = 70.0. EI-MS: m/z (%) = 281 (2) [M$^+$ − K], 224 (78) [M$^+$ − tBuK], 153 (73) [Me$_4$C$_5$PH$_2$], 74 (23) [H$_2$NEt$_2$]. C$_{17}$H$_{31}$KNP (319.51): calcd. C 63.91, H 9.78, N 4.38; found C 63.78, H 9.63, N 4.20.

[tBuC$_5$H$_3$−PtBu(NEt$_2$)]K (26): Obtained from [tBuCp−PtBu(NEt$_2$)] (**21**) (3.48 g, 12.38 mmol) and Ph$_2$CHK(THF) (3.44 g, 12.38 mmol). Yield > 95%. ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 0.93 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, −NCH$_2$*CH$_3$*), 1.0 (d, $^3J_{HP}$ = 12.5 Hz, 9 H, tBuP), 1.25 (d, $^5J_{HP}$ = 6.6 Hz, 9 H, tBuC$_5$H$_3$), 3.0 (m, 4 H, −N*CH$_2$*CH$_3$), 5.73 (m, 1 H, tBuC$_5$H$_3$), 6.55 (m, 1 H, tBuC$_5$H$_3$), 7.17 (m, 1 H, tBuC$_5$H$_3$). ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF): δ = 12.3 (CH$_3$, tBuC$_5$H$_3$), 14.8 (d, $^3J_{C,P}$ = 3 Hz, −NCH$_2$*CH$_3$*), 28.3 (d, $^2J_{C,P}$ = 16 Hz, CH$_3$, tBuP), 43.6 (d, $^2J_{C,P}$ = 15.2 Hz, −N*CH$_2$*CH$_3$), 46.4 (C, tBu), 58.1 (d, $J_{C,P}$ = 28 Hz, C, tBuP), 125.8, 126.5, 127.9 (CH, tBuC$_5$H$_3$), 128.0, 129.5 (C, tBuC$_5$H$_3$). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ = 76.0. EI-MS: m/z (%) = 281 (2) [M$^+$ − K], 224 (12) [M$^+$ − (K + tBu)], 153 (13) [tBuC$_5$H$_3$PH$_2$], 57 (5) [tBu]. C$_{17}$H$_{31}$KNP (319.51): calcd. C 63.91, H 9.78, N 4.38; found C 63.67, H 9.54, N 4.19.

[Ind−PtBu(NEt$_2$)]K (27): Obtained from [Ind−PtBu(NEt$_2$)] (**12**) (5.14 g, 18.68 mmol) and Ph$_2$CHK(THF) (5.2 g, 18.68 mmol). Yield > 95%. ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 0.91 (t, $^3J_{H,H}$ = 7 Hz, 6 H, −NCH$_2$*CH$_3$*), 1.16 (d, $^3J_{HP}$ = 12 Hz, 9 H, tBuP), 3.1 (m, $^3J_{H,H}$ = 7 Hz, 4 H, −N*CH$_2$*CH$_3$), 6.11 (d, $J_{H,H}$ = 3.5 Hz, 1 H, Ind), 6.47 (q, $J_{H,H}$ = 4 Hz, 2 H, Ind), 7.0 (t, $J_{H,H}$ = 7 and 1.5 Hz, 1 H, Ind), 7.28 (d, $J_{H,H}$ = 7 Hz, 1 H, Ind), 7.78 (d, $J_{H,H}$ = 7 Hz, 1 H, Ind). ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF): δ = 15.3 (d, $^3J_{C,P}$ = 3.7 Hz, −NCH$_2$*CH$_3$*), 29.4 (d, $^2J_{C,P}$ = 16.7 Hz, CH$_3$, tBuP), 33.9 (d, $^2J_{C,P}$ = 12.9 Hz, −N*CH$_2$*CH$_3$), 46.3 (d, $J_{C,P}$ = 16.2 Hz, C, tBuP), 98.0 (d, $^2J_{C,P}$ = 2.7 Hz, CH, Ind), 113.7 (d, $^3J_{C,P}$ = 1.4 Hz, CH, Ind), 113.8 (CH, Ind), 118.5 (d, $^3J_{C,P}$ = 1.8 Hz, CH, Ind), 119.0 (CH, Ind), 123.4 (d, $^2J_{C,P}$ = 2.7 Hz, C, Ind), 131.7 (d, $J_{C,P}$ = 8.3 Hz, C, Ind), 136.6 (CH, Ind), 137.3 (C, Ind). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ = 60.1. EI-MS: m/z (%) = 146 (100), [tBuPN(CH$_3$)Et], 115 (41) [Ind], 74 (30) [H$_2$NEt$_2$], 58 (16) [tBuH], 39 (2) [K$^+$]. C$_{21}$H$_{33}$KNP (313.46): calcd. C 75.42, H 8.72, N 3.51; found C 75.05, H 8.81, N 3.50.

[Flu−PtBu(NEt$_2$)]K (28): Obtained from [Flu−PtBu(NEt$_2$)] **17** (4.15 g, 12.77 mmol) and PhCH$_2$K (1.66 g, 12.77 mmol). Yield > 95%. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 0.9 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, −NCH$_2$*CH$_3$*), 1.09 (d, $^2J_{HP}$ = 12.2 Hz, 9 H, tBuP), 3.03 (m, 4 H, −N*CH$_2$*CH$_3$), 6.55−8.39 (several m, 8 H, Flu). ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]THF): δ = 14.1 (d, $^3J_{C,P}$ = 3 Hz, −NCH$_2$*CH$_3$*), 28.4 (d, $^1J_{C,P}$ = 22.3 Hz, CH$_3$, tBuP), 30.0 (d, $^1J_{C,P}$ = 27.3 Hz, C, tBuP), 34.7 (d, $^2J_{C,P}$ = 15 Hz, −N*CH$_2$*CH$_3$), 47.1 (d, $^1J_{C,P}$ = 40 Hz, C, Flu), 119.9, 120.0, 120.4 (CH, Flu), 121.2 (d, $J_{C,P}$ = 4.1 Hz, CH, Flu), 125.4 (d, $J_{C,P}$ = 6.5 Hz, CH, Flu), 125.5, 125.6, 126.2 (CH, Flu), 126.6 (C, Flu), 127.1 (d, $J_{C,P}$ = 2.7 Hz, C, Flu), 142.1 (d, $J_{C,P}$ = 7.9 Hz, C, Flu), 142.5 (d, $J_{C,P}$ = 4.1 Hz, C, Flu). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ = 70.9. EI-MS: m/z (%) = 325 (35) [M$^+$ − KCH$_3$], 310 (83) [M$^+$ − (K + 2 CH$_3$)], 39 (46) [K$^+$]. C$_{22}$H$_{31}$NP (379.57): calcd. C 69.62, H 8.23, N 3.69; found C 69.24, H 8.11, N 3.52.

[{Ind−PtBu(NEt$_2$)}$_2$CEt$_2$]K$_2$(THF)$_2$ (29): Obtained from [{Ind−PtBu(NEt$_2$)}$_2$CEt$_2$][31] (3.63 g, 5.87 mmol) and Ph$_2$CHK(THF) (3.27 g, 11.74 mmol). Isolated 4.0 g, yield 81%. ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 0.74−1.12 (several resonances, tBu and −NCH$_2$*CH$_3$*), 3.0 (m, 4 H, −N*CH$_2$*CH$_3$), 6.0−7.61 (several m, 6 H, Ind). ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF): δ = 15.5 (d, $^3J_{C,P}$ = 3 Hz, −NCH$_2$*CH$_3$*), 29.7 (d, $^2J_{C,P}$ = 16.9 Hz, CH$_3$, tBu), 34.4 (d, $^2J_{C,P}$ = 15.9 Hz, −N*CH$_2$*CH$_3$), 46.4 (d, $^1J_{C,P}$ = 27.1 Hz, C, tBuP), 110.0−130.0 (C and CH resonances, Ind). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF): δ = 57.1. EI-MS: m/z (%) = 341 (16) [M$^+$ − MeInd(tBu)PNEt$_2$K], 160 (2) [tBuPNEt$_2$], 115 (87) [Ind], 57 (42) [tBu], 39 (100) [K$^+$]. C$_{47}$H$_{74}$KN$_2$O$_2$P$_2$ (839.26): calcd. C 67.26, H 8.89, N 3.34; found C 67.44, H 9.10, N 3.18.

[Me$_3$SiC$_{13}$H$_8$−PtBu(NSiMe$_3$$t$Bu)] (30): Obtained in situ from [Flu−PtBu(NHtBu)] (**18**) (1.44 g, 4.42 mmol) in THF, nBuLi (6 mL, 9 mmol) and Me$_3$SiCl (1.67 mL, 13.26 mmol). Isolated 1.41 g, yield 67%. ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = −0.04 (s, 9 H, Me$_3$Si), 0.01 (s, 9 H, Me$_3$Si), 0.33 (d, $^3J_{HP}$ = 10.3 Hz, 9 H, tBuP), 0.47 (s, 9 H, tBuN), 7.05−7.44 (m, 4 H, Flu), 7.51 (m, 2 H, Flu), 7.94 (m, 2 H, Flu).

[(Me$_3$Sn)Me$_4$C$_5$−PtBu(NEt$_2$)] (31): Obtained from [Me$_4$Cp−PtBu(NEt$_2$)]K (**25**) (4.58 g, 14.36 mmol) and Me$_3$SnCl (2.9 g,

> 14.36 mmol). Yield > 95%. ^{1}H NMR (400 MHz, [D$_6$]benzene): δ = 0.08, 0.24, 0.26 (s, broad s, s, 9 H, Me_3Sn-), 1.04 (d, $^3J_{HP}$ = 10 Hz, 9 H, *t*BuP), 1.06 (t, $^3J_{H,H}$ = 8 Hz, 6 H, $-NCH_2CH_3$), 1.88 (s, 3 H, CH_3, Me_4C_5), 1.92 (s, 3 H, CH_3, Me_4C_5), 2.18 (s, 3 H, CH_3, Me_4C_5), 2.24 (s, 3 H, CH_3, Me_4C_5), 3.24 (m, $^3J_{HP}$ = 7.1 Hz, 4 H, $-NCH_2CH_3$). ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene): δ = −7.2 (d, $^5J_{C,P}$ = 2.7 Hz, CH_3, Me_3Sn-), 1.3 (CH_3, Me_3Sn-), 11.1 ($-NCH_2CH_3$), 11.5, 14.0, 14.2, 15.9 (CH_3, Me_4C_5), 29.6 (d, $^2J_{C,P}$ = 16.8 Hz, CH_3, *t*BuP), 38.4 (d, $^2J_{C,P}$ = 17.2 Hz, $-NCH_2CH_3$), 46.8 (d, C, *t*BuP, $^2J_{C,P}$ = 25.8 Hz), 48.0 (d, $J_{C,P}$ = 18.9 Hz, C, Me_4C_5), 130.9 (d, $J_{C,P}$ = 6 Hz, C, Me_4C_5), 131.3 (d, $J_{C,P}$ = 4.8 Hz, C, Me_4C_5), 132.9, 133.2 (C, Me_4C_5). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 85.0. EI-MS: *m*/*z* (%) = 254 (8) [$Me_2C_5SnMe_3$], 240 (46) [$Me_2C_5SnMe_2$], 121 (92) [Me_4C_5], 120 (100) [$Me_3C_5CH_2$], 72 (38) [NEt_2], 57 (46) [*t*Bu]. $C_{20}H_{40}NPSn$ (444.2): calcd. C 54.08, H 9.08, N 3.15; found C 54.19, H 8.92, N 3.01.

[(Me$_3$Sn)*t*BuC$_5$H$_3$−P*t*Bu(NEt$_2$)] (32): Obtained from [*t*BuCp−P*t*Bu(NEt$_2$)]K (**26**) (1.0 g, 3.12 mmol) and Me_3SnCl (0.7 g, 3.12 mmol). Yield > 95%. *Mixture of Isomers:* ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 0.15 (s, 9 H, Me_3Sn-), 0.92 (t, $^3J_{H,H}$ = 7 Hz, $-NCH_2CH_3$), 1.32 (d, $^3J_{HP}$ = 12.1 Hz, 9 H, *t*BuP), 2.98 (m, 4 H, $-NCH_2CH_3$), 4.28 (d, 1 H, *t*BuC$_5$H$_3$), 7.28−7.42 (m, 3 H, *t*BuC$_5$H$_3$), 6.3−7.1 (several m, 2 H, *t*BuC$_5$H$_3$). ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = −7.5 (d, $^3J_{C,P}$ = 5 Hz, CH_3, Me_3Sn-), 12.2 (CH_3, *t*BuC$_5$H$_3$), 14.8 (2 d, $^3J_{C,P}$ = 2.7 Hz, $-NCH_2CH_3$), 28.3 (2 d, $^2J_{C,P}$ = 16.1 Hz, CH_3, *t*BuP), 43.1 (C, *t*BuC$_5$H$_3$), 45.7 (d, $^2J_{C,P}$ = 15.6 Hz, $-NCH_2CH_3$), 61.0 (d, $J_{C,P}$ = 28.9 Hz, C, *t*BuP), 123.8, 124.9 (CH, *t*BuC$_5$H$_3$), 144.4, 152.1, 152.2 (C, *t*BuC$_5$H$_3$). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 71.8. EI-MS: *m*/*z* (%) = 445 (7) [M$^+$], 388 (29) [M$^+$ − *t*Bu], 317 (61) [M$^+$ − ($HNEt_2$ + *t*Bu)], 165 (100) [$SnMe_3$], 57 (43) [*t*Bu]. $C_{20}H_{40}NPSn$ (445.19): calcd. C 54.08, H 9.08, N 3.15; found C 54.16, H 8.84, N 3.20.

[Me$_3$SnC$_9$H$_6$−P*t*Bu(NEt$_2$)] (33): Obtained from [Ind−P*t*Bu(NEt$_2$)]K (**27**) (4.15 g, 13.24 mmol) and Me_3SnCl (2.7 g, 14.0 mmol). Yield > 95%. *Mixture of Isomers:* ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = −0.13, −0.08 (2 s, 9 H, Me_3Sn-), 1.05 (t, $^3J_{H,H}$ = 5.7 Hz, $-NCH_2CH_3$), 1.36, 1.29 (d, $^3J_{HP}$ = 12.2 Hz, 9 H, *t*BuP), 3.25 (m, 4 H, $-NCH_2CH_3$), 4.27, 4.03 (d, 1 H, Ind), 7.06 (m, 1 H, Ind), 7.28−7.42 (m, 3 H, Ind), 8.55 (m, 1 H, Ind). ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = −9.1 (d, $^3J_{C,P}$ = 1.3 Hz, CH_3, Me_3Sn-), 15.3 (2 d, $^3J_{C,P}$ = 3.2 Hz, $-NCH_2CH_3$), 28.3 (2 d, $^1J_{C,P}$ = 16 Hz, CH_3, *t*BuP), 33.8 (d, $J_{C,P}$ = 17 Hz, C, *t*BuP), 45.8 (CH, Ind), 46.6, 46.3 (d, $^2J_{C,P}$ = 15.6 Hz, $-NCH_2CH_3$), 121.9 (CH, Ind), 122.1 (C, Ind), 123.7, 124.0, 134.9, 137.9, 145.2, 145.4, 145.5, 145.6 (CH, Ind), 145.7, 145.9, 146.0, 146.2 (C, Ind). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 63.2, 64.0. EI-MS: *m*/*z* (%) = 438 (5) [M$^+$], 382 (29) [M$^+$ − *t*Bu], 368.7 (1) [M$^+$ − NEt_2], 275 (9) [L$^+$], 202 (2) [L$^+$ − NEt_2], 165 (93) [$SnMe_3$], 161 (41) [*t*BuP(H)NEt_2]. $C_{20}H_{34}NPSn$ (438.16): calcd. C 54.82, H 7.82, N 3.20; found C 54.45, H 7.90, N 3.01.

[Me$_3$SnC$_{13}$H$_8$−P*t*Bu(NEt$_2$)] (34): Obtained from [Flu−P*t*Bu(NEt$_2$)]K (**28**) (0.5 g, 1.37 mmol) and Me_3SnCl (0.3 g, 1.5 mmol). Yield > 95%. ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 0.03 (s, 9 H, Me_3Sn-), 0.73 (d, $^3J_{HP}$ = 12.6 Hz, 9 H, *t*BuP), 1.11 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, $-NCH_2CH_3$), 3.36 (m, 4 H, $-NCH_2CH_3$), 7.29−7.37 (m, 4 H, Flu), 7.93−7.98 (br. m, 2 H, Flu), 8.2 (m, 2 H, Flu). ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = −8.15 (d, $^3J_{C,P}$ = 3.2 Hz, CH_3, Me_3Sn-), 15.18 ($-NCH_2CH_3$), 29.9 (d, $^2J_{C,P}$ = 16 Hz, CH_3, *t*BuP), 30.8 (d, $^2J_{C,P}$ = 15.1 Hz, $-NCH_2CH_3$), 39.0 (d, $J_{C,P}$ = 28.4 Hz, C, *t*BuP), 120.0, 120.5, 125.9, 126.0 (CH, Flu), 137.7, 139.0, 148.1, 148.7, 149.1 (C, Flu). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 102.9. $C_{20}H_{34}NPSn$ (488.22): calcd. C 59.04, H 7.43, N 2.87; found C 59.19, H 7.60, N 2.71.

[Me$_3$SnC$_9$H$_6$−P*t*Bu(NH*t*Bu)] (35): Me_3SnNEt_2 (2.36 g, 10.0 mmol) was added at 0 °C to a solution of [Ind−P*t*Bu(NH*t*Bu)] (**13**) (2.75 g, 10 mmol) in 100 mL of diethyl ether. Then the reaction mixture was stirred for 1 h, while warming to room temperature. The solvent and diethylamine were removed under vacuum. Yield > 95%. ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 0.03 (s, $^2J_{HSn}$ = 54 Hz, 9 H, Me_3Sn-),1.22 (d, $^3J_{HP}$ = 12.9 Hz, 9 H, *t*BuP), 1.35 (s, 9 H, *t*BuN), 1.96−1.90 (m, 1 H, −NH), 4.1 (s, 1 H, Ind), 6.79 (m, 1 H, Ind), 7.29−7.37 (m, 2 H, Ind), 7.39−7.48 (m, 1 H, Ind), 8.14−8.16 (m, 1 H, Ind). ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = −6.7 (CH_3, Me_3Sn-), 29.1 (d, $^2J_{C,P}$ = 15.3 Hz, *t*BuP), 34.2 (d, $^1J_{C,P}$ = 17.8 Hz, C, *t*BuP), 34.5 (d, $^3J_{C,P}$ = 8.8 Hz, *t*BuN), 47.7 (CH, Ind), 52.9 (d, $^2J_{C,P}$ = 15.9 Hz, C, *t*BuN), 123.6, 124.8, 126.1, 127.3, 127.7 (CH, Ind), 128.8, 139.9, 140.9 (C, Ind). ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene): δ = 22.3. $C_{20}H_{36}NPSn$ (440.17): calcd. C 54.57, H 8.24, N 3.18; found C 54.66, H 8.13, N 3.01.

[{Me$_4$C$_5$−P*t*Bu(NEt$_2$)}TiCl$_3$] (36): All of the $TiCl_4(THF)_2$ (0.64 g, 1.93 mmol) in 20 mL of toluene was immediately added to a solution of [(Me_3Sn)Me_4C_5−P*t*Bu(NEt_2)] (**31**) (0.86 g, 1.93 mmol) in 30 mL of toluene at −50 °C. The reaction mixture was then stirred for 3 h, while warming to room temperature. After that, the reaction mixture was additionally stirred for another 5 h at 80 °C. The solvent was removed under vacuum. The product was extracted with pentane. Isolated 0.31 g (0.7 mmol), deep red solid (yield 38%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.11 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, $-NCH_2CH_3$), 1.14 (d, $^3J_{HP}$ = 14 Hz, 9 H, *t*BuP), 2.33 (s, 3 H, CH_3, Me_4C_5), 2.39 (d, $^4J_{HP}$ = 0.5 Hz, 3 H, CH_3, Me_4C_5), 2.61 (d, $^4J_{HP}$ = 0.7 Hz, 3 H, CH_3, Me_4C_5), 2.7 (s, 3 H, CH_3, Me_4C_5), 3.24 (m, 4 H, $-NCH_2CH_3$). ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2): δ = 14.5 ($-NCH_2CH_3$), 15.0, 17.8, 18.1, 18.8 (CH_3, Me_4C_5), 29.7 (d, $J_{C,P}$ = 18.1 Hz, CH_3, *t*BuP), 37.7, 38.0 ($-NCH_2CH_3$), 47.4 (d, $J_{C,P}$ = 17.4 Hz, C, *t*BuP), 125.4 (d, $J_{C,P}$ = 23.5 Hz, C, Me_4C_5), 128.9 (d, $J_{C,P}$ = 32.9 Hz, C, Me_4C_5), 140.0 (d, $J_{C,P}$ = 4.5 Hz, C, Me_4C_5), 141.3 (d, $J_{C,P}$ = 2.2 Hz, C, Me_4C_5), 143.2 (C, Me_4C_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 77.2. EI-MS: *m*/*z* (%) = 378 (3) [M$^+$ − (*t*Bu + H)], 187 (15) [$C_6H_{10}TiCl$], 153 (6) [$TiCl_3$], 121 (25) [Me_4C_5H], 73 (42) [$HNEt_2$], 58 (100) [*t*BuH]. $C_{17}H_{31}Cl_3NPTi$ (433.07): calcd. C 46.98, H 7.19, N 3.22; found C 46.88, H 7.24, N 3.15.

[{Me$_4$C$_5$−P*t*Bu(NEt$_2$)}ZrCl$_3$] (37): Obtained from [(Me_3Sn)-Me_4C_5−P*t*Bu(NEt_2)] (**31**) (0.57 g, 1.3 mmol) and $ZrCl_4(THF)_2$ (0.49 g, 1.3 mmol), using the same procedure as for the preparation of [{Me_4C_5−P*t*Bu(NEt_2)}$TiCl_3$] (**36**). Isolated 0.15 g (0.32 mmol), yellow solid (yield 25%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.10 (t, $^3J_{H,H}$ = 7 Hz, 6 H, $-NCH_2CH_3$), 1.16 (d, $^3J_{HP}$ = 14.2 Hz, 9 H, *t*BuP), 2.15 (s, 3 H, CH_3, Me_4C_5), 2.16 (s, 3 H, CH_3, Me_4C_5), 2.45 (s, 3 H, CH_3, Me_4C_5), 2.52 (s, 3 H, CH_3, Me_4C_5), 3.19 (m, 4 H, $-NCH_2CH_3$). ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2): δ = 12.8 ($-NCH_2CH_3$), 13.9, 15.7, 16.1, 17.5 (CH_3, Me_4C_5), 29.5 (d, $J_{C,P}$ = 18.9 Hz, CH_3, *t*BuP), 37.0, 37.5 ($-NCH_2CH_3$), 47.6 (d, $J_{C,P}$ = 17 Hz, C, *t*BuP), 128.4, 128.2 (C, Me_4C_5), 129.0 (br. resonance, C, Me_4C_5), 132.5 (d, $J_{C,P}$ = 3.8 Hz, Me_4C_5), 132.7 (br. resonance, C, Me_4C_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 73.2. EI-MS: *m*/*z* (%) = 346 (1) [M$^+$ − $C_8H_{19}N$], 224 (27) [M$^+$ − $C_{12}H_{27}N$], 153 (40) [Me_4C_5P], 121 (100) [Me_4C_5H], 106 (7) [Me_4C_5H − Me], 73 (5) [$HNEt_2$] 57 (56) [*t*Bu]. $C_{17}H_{31}Cl_3NPZr$ (475.03): calcd. C 42.72, H 6.54, N 2.93; found C 42.57, H 6.33, N 2.81.

[{*t*BuC$_5$H$_3$−P*t*Bu(NEt$_2$)}TiCl$_3$] (38): Obtained from [(Me_3Sn)*t*BuC$_5$H$_3$−P*t*Bu(NEt_2)] (**32**) (0.57 g, 1.28 mmol) and

$TiCl_4(THF)_2$ (0.42 g, 1.28 mmol) using the same procedure as for the preparation of [{Me_4C_5−P*t*Bu(NEt$_2$)}$TiCl_3$] (**36**). Isolated 0.16 g (0.37 mmol), deep red solid (yield 30%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, −NCH$_2$*CH$_3$*), 1.14 (d, $^3J_{HP}$ = 13.7 Hz, 9 H, *t*BuP), 1.40 (d, J_{HP} = 1 Hz, 9 H, CH_3, *t*BuC_3H_5), 3.16 (m, 4 H, −N*CH$_2$*CH$_3$), 6.93−7.30 (several m, 3 H, *t*BuC_3H_5). ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2): δ = 15.5 (CH_3, −NCH$_2$*CH$_3$*), 15.7 (CH_3, *t*BuC_3H_5), 28.6 (d, $J_{C,P}$ = 17 Hz, CH_3, *t*BuP), 35.2, 35.3 (−N*CH$_2$*CH$_3$), 43.6 (C, *t*BuC_3H_5), 47.2 (d, $J_{C,P}$ = 15.5 Hz, C, *t*BuP), 125.1, 128.4, 129.2 (CH, *t*BuC_3H_5), 151.0 (d, $J_{C,P}$ = 21 Hz, C, *t*BuC_3H_5) 159.5 (C, *t*BuC_3H_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 88.4, 88.5. EI-MS: *m*/*z* (%) = 361 (2) [M^+ − NEt_2], 304 (12) [M^+ − $C_8H_{19}N$], 281 (35) [$C_{15}H_{32}N$], 160 (4) [*t*BuPNEt$_2$], 121 (100) [*t*BuC_5H_3], 72 (54) [NEt_2], 57 (73) [*t*Bu]. $C_{17}H_{31}Cl_3NPTi$ (433.07): calcd. C 46.98, H 7.19, N 3.22; found C 47.11, H 7.29, N 3.05.

[{*t*BuC_5H_3−P*t*Bu(Cl)}$TiCl_3$] (39): $TiCl_4$ (0.45 mL, 4.09 mmol) was slowly added at −80°C to a solution of [*t*BuC_5H_3−P*t*Bu(Cl)] (**6**) (1.0 g, 4.1 mmol) in 30 mL of hexane; after 1 min of stirring, Et_3N (0.57 mL, 4.1 mmol) was added. The reaction mixture was stirred for 4 h, while warming to room temperature. The ammonium salt precipitate was removed by filtration. All volatiles were removed under vacuum to give the crude product. Yield according to ^{1}H and ^{31}P NMR spectra was 98%. An analytically pure product was obtained, after two times of washing with cold (−50 °C) pentane, as an orange solid with 40% yield. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.09, 1.05 (2 d, J_{HP} = 14.3 Hz, J_{HP} = 14.4 Hz, 9 H, *t*BuP), 1.4 (s, 9 H, *t*Bu), 7.0 (m, 6 H, *t*BuC_3H_5), 7.02−7.1 (2 m, CH, *t*BuC_3H_5), 7.25 (m, CH, *t*BuC_3H_5), 7.32 (m, CH, *t*BuC_3H_5). ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 25.2 (CH_3, *t*BuC_3H_5), 30.8 (d, $^2J_{C,P}$ = 12.9 Hz, CH_3, *t*BuP), 35.2 (d, $^4J_{C,P}$ = 2.6 Hz, C, *t*Bu), 36.3 (d, $J_{C,P}$ = 25.4 Hz, C, *t*BuP), 122.3 (d, $^2J_{C,P}$ = 2.9 Hz, CH, *t*BuC_3H_5), 122.3 (d, $^2J_{C,P}$ = 2.9 Hz, CH, *t*BuC_3H_5), 125.4 (d, $J_{C,P}$ = 4.8 Hz, C, *t*BuC_3H_5), 125.9 (CH, *t*BuC_3H_5), 123.4 (d, $^2J_{C,P}$ = 3.3 Hz, CH, *t*BuC_3H_5), 126.3 (C, *t*BuC_3H_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 105.4, 106.4. EI-MS: *m*/*z* (%) = 362 (1) [M^+ − Cl], 270 (2) [$C_9H_{13}Cl_2TiP$], 244 (3) [*t*BuC_5H_3(*t*Bu)PCl], 121 (10) [*t*BuC_5H_3], 57 (100) [*t*Bu]. $C_{13}H_{21}Cl_4PTi$ (397.37): calcd. C 39.23, H 5.32; found C 39.05, H 5.09.

[{(C_5H_4−P*t*Bu(Cl)]$_2$CMe$_2$}{$TiCl_3$}$_2$] (40): Obtained from [{C_5H_4−P*t*Bu(Cl)}$_2$CMe$_2$] (**11**) (3.98 g, 9.5 mmol), $TiCl_4$ (2.09 mL, 19.1 mmol) and Et_3N (2.66 mL, 19.1 mmol), using the same procedure as for the preparation of [{*t*BuC_5H_3−P*t*Bu(Cl)}$TiCl_3$] (**39**). According to ^{1}H and ^{31}P NMR spectra the yield was 90%. A product was isolated as a deep green solid. *Mixture of Isomers:* ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.87−1.0 (several d, 9 H, *t*BuP),

Table 1. Crystal data and structure refinement for **15**

Empirical formula[a]	$C_{23}H_{38}NP$
Formula mass	359.51
Crystal size [mm]	0.40 × 0.20 × 0.15
Temperature [K]	223(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions [Å, °]	a = 7.768(1), b = 22.196(1), c = 12.8267(10), β = 91.14(1)
Volume [Å^3]	2211.2(3)
Z	4
Calculated density [g/cm^3]	1.080
Absorption coefficient [mm^{-1}]	0.130
F(000)	792
Θ-range for data collection [°]	2.43 to 23.41
Index ranges	$-8 \le h \le 0$, $-24 \le k \le 0$, $-14 \le l \le 14$
Reflections collected/unique	3502/3235, [R(int) = 0.0682]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3235/0/280
Goodness-of-fit on F^2	1.100
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0754, $wR2$ = 0.2332
R indices (all data)	$R1$ = 0.1357, $wR2$ = 0.2678
Largest diff. peak and hole [e/Å^3]	0.454 and −0.489

[a] Data collection and cell refinement has been carried out with an Enraf Nonius CAD4 four-circle diffractometer using CAD4-EXPRESS software. Data reduction and Lorentz and polarisation corrections were undertaken using the XCAD4 programme (K. Harms, **1993**). For structure solution SHELXS-96 and structure refinement SHELXL-96 (both G. M. Sheldrick, **1996**) were used. Molecular graphics: ORTEP III. After data reduction the data set has been checked for systematic absence violations. Due to weak absence violations *h0l*: $l \neq 2n$ for compound **15** two space groups should be taken into account, $P2_1$ and $P2_1/c$. The structure was first solved by direct methods in the chiral space group $P2_1$ and a structural model including all non-hydrogen atoms was refined isotropically. A search for additional symmetry elements (PLATON: A. Speck, **1990**) showed that a slide mirror plane parallel to the crystallographic axis c exists. The "zero point" was placed in the centre of inversion and the structure was refined in the centrosymmetric space group $P2_1/c$, after all symmetrically dependent atoms had been eliminated. The hydrogen atoms were placed at a calculated position and refined in a riding model.

Table 2. Crystal data and structure refinement for **36**

Empirical formula[a]	$C_{17}H_{31}Cl_3NPTi$
Formula mass	434.65
Crystal size [mm]	0.36 × 0.21 × 0.12
Temperature [K]	203(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions [Å, °]	a = 9.351(2), b = 15.637(2), c = 14.732(1), β = 91.39(1)
Volume [Å^3]	2153.5(5)
Z	4
Calculated density [g/cm^3]	1.341
Absorption coefficient [mm^{-1}]	0.843
F(000)	912
Θ-range for data collection [°]	2.54 to 22.55
Index ranges	$0 \le h \le 10$, $-16 \le k \le 0$, $-15 \le l \le 15$
Reflections collected/unique	3007/2807, [R(int) = 0.0488]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2807/0/217
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0550, $wR2$ = 0.1168
R indices (all data)	$R1$ = 0.1007, $wR2$ = 0.1365
Largest diff. peak and hole [e/Å^3]	0.906 and −0.751

[a] Data collection and cell refinement has been carried out with an Enraf−Nonius CAD4 four-circle diffractometer using CAD4-EXPRESS software. Data reduction and Lorentz and polarisation corrections were undertaken using the XCAD4 programme (K. Harms, **1997**). For the structure solution SHELXS-97 and structure refinement SHELXL-97 (both G. M. Sheldrick, **1997**) were used. Molecular graphics: ORTEP III. An analytical absorption correction based on face indexing was applied to the data set. Hydrogen atoms were placed at calculated positions and refined in a riding model.

2.1 (s, 3 H, CH_3, CMe_2), 6.99−7.04 (several m, 1 H, Cp), 7.09−7.15 (several m, 1 H, Cp). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 95.3, 94.4, 95.8, 101.3, 102.4, 102.5 (2 signals), 102.7, 103.0, 103.3(2 signals), 103.4, 103.5, 103.6, 104.0, 104.3. EI-MS: *m*/*z* (%) = 534 (12) [$M^+ - TiCl_4$], 442 (22) [$M^+ - TiCl_3 - t$BuPCl], 386 (30) [$M^+ - Cp(t\text{Bu})PTiCl_4$], 318 (92) [$Cp(t\text{Bu})PTiCl_3 - H$], 57 (100) [*t*Bu].

[{(C_5H_3−P*t*Bu(Cl)]$_2$$CMe_2$}$TiCl_2$] (41): Obtained from [{$C_5H_4$−P*t*Bu(Cl)}$_2$$CMe_2$] (**11**) (4.79 g, 11.5 mmol), $TiCl_4$ (1.25 mL, 11.5 mmol) and Et_3N (3.2 mL, 23.0 mmol) using the same procedure as for the preparation of [{*t*BuC_5H_3−P*t*Bu(Cl)}$TiCl_3$] (**39**). According to ^1H and ^{31}P NMR spectra the yield was 90%. A product was isolated as a deep red solid. *Mixture of Isomers:* ^1H NMR (400 MHz, CD_2Cl_2): δ = 0.85−1.5 (several m, *t*BuP), 1.7−1.9 (several m, CH_3, CMe_2), 5.3−5.92 (several m, Cp), 7.14−7.24 (several m, Cp). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 96.2, 96.6, 96.8, 97.5, 101.7, 103.0, 103.2, 103.7.

[{*t*BuC_5H_3−P*t*Bu(N*t*Bu)}$TiCl_2$] (42): A suspension of Li[NH*t*Bu] (0.03 g, 0.37 mmol) and Et_3N (0.052 mL, 0.37 mmol) were immediately added, −78 °C, to a solution of [{*t*BuC_5H_3−P*t*Bu(Cl)}$TiCl_3$] (**39**) (0.15 g, 0.37 mmol) in 20 mL of toluene. The reaction mixture was stirred for 12 h, while warming to room temperature. Then the precipitated LiCl and Et_3NHCl were removed by filtration. The filtrate was concentrated under vacuum. The product was taken up in pentane. Isolated 0.13 g (0.33 mmol), deep red solid (yield 89%). *Mixture of 2 Isomers (1:3):* ^1H NMR (200 MHz, CD_2Cl_2): δ = 1.24 (*major*), 1.20 (*minor*) [2 d, $^3J_{HP}$ = 14.4 Hz (*both isomers*), 9 H, *t*BuP], 1.30 (*major*), 1.27 (*minor*) [2 d, $^6J_{HP}$ = 3.7 Hz (*major*), 3.5 Hz (*minor*), 9 H, CH_3, *t*BuC_5H_3], 1.45 (*minor*), 1.42 (*major*) [2 d, $^4J_{HP}$ = 0.7 Hz (*both isomers*), 9 H, *t*BuN], 6.95−7.85 (6 m, total 3 H, *t*BuC_5H_3). *Both Isomers:* $^{13}C\{^1H\}$ NMR (50 MHz, [D_6]benzene): δ = 15.0, 15.1, 15.2, 15.3 (CH_3, *t*BuN and *t*Bu), 29.0 (d, $J_{C,P}$ = 17 Hz, CH_3, *t*BuP), 29.6 (d, $J_{C,P}$ = 18.5 Hz, CH_3, *t*BuP), 47.0 (d, $J_{C,P}$ = 17 Hz, C, *t*BuP), 47.5 (d, $J_{C,P}$ = 16.1 Hz, C, *t*BuP), 53.1, 53.2 (C, *t*Bu), 61.9, 62.8 (C, *t*BuN), 134.6 (d, $J_{C,P}$ = 1.5 Hz, CH, *t*BuC_5H_3), 135.7 (d, $J_{C,P}$ = 1.5 Hz, CH, *t*BuC_5H_3), 135.8 (d, $J_{C,P}$ = 4.5 Hz, CH, *t*BuC_5H_3), 135.9 (d, $J_{C,P}$ = 4 Hz, CH, *t*BuC_5H_3), 141.7 (d, $J_{C,P}$ = 36 Hz, CH, *t*BuC_5H_3), 142.4 (d, $J_{C,P}$ = 34 Hz, CH, *t*BuC_5H_3), 145.1 (d, $J_{C,P}$ = 1.5 Hz, C, *t*BuC_5H_3), 145.3 (C, *t*BuC_5H_3), 150.5 (d, $J_{C,P}$ = 30 Hz, C, *t*BuC_5H_3), 151.5 (d, $J_{C,P}$ = 29 Hz, C, *t*BuC_5H_3). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 45.9 (*major*), 51.1 (*minor*). EI-MS: *m*/*z* (%) = 340 (4) [$M^+ - t$Bu], 283 (15) [$M^+ - 2\ t$Bu], 226 (35) [$M^+ - 3\ t$Bu], 121 (100) [*t*BuC_5H_3], 57 (100) [*t*Bu]. $C_{17}H_{30}Cl_2NPTi$ (397.09): calcd. C 51.28, H 7.59, N 3.52; found C 51.13, H 7.68, N 3.44.

Polymerisation of Ethylene: A glass autoclave was charged with 50 mL of toluene and 0.5 mL of triisobutylaluminium, then thermostatted for 30 min and saturated with ethylene (3 bar) for another 30 min. The catalyst was generated by treatment of the corresponding complex with MAO [10% solution in toluene, Al/(Ti or Zr) ratio was either 500 or 2000] and preformed over 1 h in an ultrasonic bath. This toluene solution was injected into the autoclave. The reaction mixture was placed under 3 bar of ethylene for 30 min with rapid stirring. The polymerisation was stopped by quenching with 50 mL of aqueous HCl/methanol (1:5, v/v). The polymer was isolated by filtration, washed subsequently with HCl solution, water, methanol, acetone and dried at 60 °C to a constant weight. All polymerisation experiments were repeated at least twice, whereby no large deviations have been observed.

X-ray Crystallographic Study: Crystallographic data for the structures reported (Tables 1 and 2) in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-162747 (**15**) and -162746 (**36**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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