Synthesis of New Cyclopentadienyl-, Indenyl- and Fluorenylphosphanes by the Reaction of Carbanions of the Cyclopentadienyl Type with Alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes

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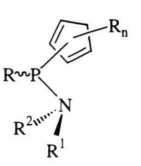
Cyclopentadienylphosphanes, Alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes, (Amino)cyclopentadienylphosphanes

A number of alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes $RP(Cl)NR^1R^2$ (**1a–o**) were synthesized starting from alkyl(aryl)dichlorophosphanes $RPCl_2$ and amines by a convenient procedure with nearly quantitative yields. The reactivity of alkyl(aryl)-*N,N*-dialkylamino(halogeno)phosphanes $RP(Hal)NR^1R^2$ (Hal = Cl, I) with cyclopentadienyl, bis(cyclopentadienyl), indenyl, bis(indenyl) and fluorenyl carbanions has been investigated. The new aminocyclopentadienylphosphanes $R_nCp(R)PNR^1R^2$ **2a–f** and **3a–c** (R_nCp = Ind, Flu, Cp_2CMe_2, Ind_2CEt_2, $Ind_2(CH_2)_2$) were characterized by spectroscopic techniques and elemental analyses. Flu(*t*-Bu)PN(H)*t*-Bu (**2f**) was characterized by X-ray diffraction analysis.

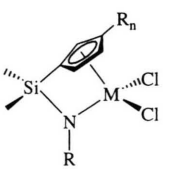
Introduction

So called CGC (Constrained Geometry Catalysts) complexes (**I**) as a new class of homogeneous olefin polymerization catalysts were reported ten years ago by researchers of Dow and Exxon [1–3]. These group 4 mono-cyclopentadienyl-amido derivatives are based on the ligand system first described by Bercaw [4] for organoscandium complexes, and are distinguished by a sterically accessible catalyst active site, which allows incorporation of other olefins into polyethylene. There is a number of reports in the literature dealing with the copolymerization of ethylene and linear α-olefins such as propene, 1-butene, 1-hexene and 1-octene [1,2] with cyclic monomers such as ethylidene-norbornene [5,6]. Additionally, when compared to bis-cyclopentadienyl metallocenes, the activated CGC catalysts are thermally more stable up to reaction temperatures of 160 °C and generally produce polymers of higher molecular weight [7]. Several types of complexes of such kind have been described up to now, *e.g.* $[Me_4Cp(SiMe_2)Nt\text{-}Bu]MCl_2$ (**I**) [1,2], $[Cp(CH_2)_2NMe]MCl_2$ [8], $[Cp(C{=}CH_2)NR]MCl_2$ [9], $[Me_4Cp(BNi\text{-}Pr_2)NPh]MCl_2$ [10] (R = Alk; M = Ti(IV), Zr(IV), Hf(IV)).

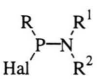
We have been exploring the synthesis of new ligands derived from the alkyl(amino)cyclopentadienylphoshanes $R_nCpP(R)NR^1R^2$ (R_n, R, R^1, R^2 = Alk, Ar or H) in an attempt to probe this class of compounds as ligands in transition metal chemistry. The choice of $R_nCpP(R)NR^1R^2$ was stimulated by the expectation that the presence of two strong σ-donors connected with the cyclopentadienyl frame could have an impact on the catalytic properties of the target complexes due to electron donating effects of the $R_2N(R)P$-moiety.



I



II



III

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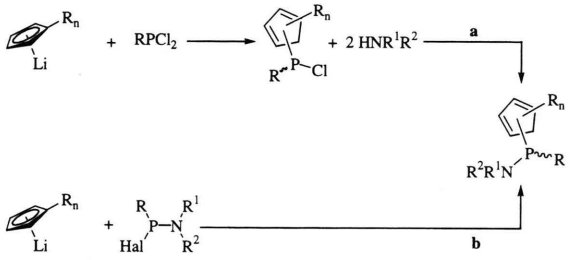
There are two main synthetic approaches to the type **II** of ligands (Scheme 1), containing a three-coordinated phosphorus atom: a) a stepwise nucleophilic substitution of the halogen atoms at the phosphorus center by cyclopentadienyl type carbanions and amines and b) the reaction of cyclopentadienyl anions with alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes (**III**). Both routes have been applied for the preparation of the ligand precursors in our work.



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

Scheme 1.

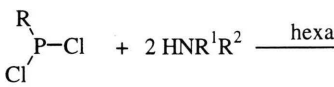
The route "a" is a common pathway to alkylamino(cyclopentadienyl)phoshanes and has been described previously in the literature [11–13]. This method is, however, confined to bulky cyclopentadienyl and alkyl substituents at the phosphorus atom.

The second route "b" for which alkyl(aryl)-chloro-*N,N*-dialkylaminophosphanes might be used as starting key-compounds has not been explored so far. It could advantageously be used for the preparation of sterically less encumbered derivatives. To the best of our knowledge, only one example of such reactions, *i.e.* that of FluLi with $Cl(Ar)PNEt_2$ leading to the corresponding $Flu(Ar)PNEt_2$ (Ar = 2,6-dimethylphenyl) in good yield, has been described in the literature [14]. Here we report the synthesis of new alkylamino-(cyclopentadienyl)phosphanes (**II**), using route "b" as a synthetic strategy, and the unexpected behavior of alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes (**III**).

Results and Discussion

It is well known that cyclopentadienylphosphanes are a thermally labile class of compounds [15]. They readily undergo Diels-Alder reactions which are promoted by the phosphanyl substituent at the cyclopentadienyl ring. To avoid an oligomerization of the target product we used bulky substituents at the phosphorus atom (*e.g.* R = *t*-Bu) and alkyl-substituted cyclopentadienes, as well as their benzocondensed analogues such as indene or fluorene, and bridged biscyclopentadienes with a carbon bridge as educts.

Generally, alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes $RP(Cl)NR^1R^2$ are easily accessible from the reaction between an alkyl(aryl)dichlorophosphane $RPCl_2$ and an amine/amide in diethyl ether [16–18] or a trimethylsilyl-substituted amine $Me_3SiNR^1R^2$ [19]. In both cases a fractional distillation had to be applied for the isolation of the product. In our work we modified the procedure [16] (see experimental part) and prepared a series of alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes $RP(Cl)NR^1R^2$ by a direct reaction of $RPCl_2$ with an amine HNR^1R^2 in hexane at low temperature (Scheme 2).



1a-o

1	**a**	**b**	**c**	**d**	**e**
R	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu
R¹	*t*-Bu	Et			Ph
R²	H	Et	$(CH_2)_5$	$(CH_2CH_2)_2O$	H

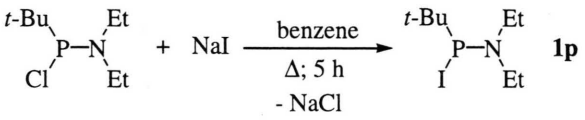
1	**f**	**g**	**h**	**i**	**j**
R	Me	Me	Me	Me	Me
R¹	*t*-Bu	Et			Ph
R²	H	Et	$(CH_2)_5$	$(CH_2CH_2)O$	

1	**k**	**l**	**m**	**n**	**o**
R	Ph	Ph	Ph	Ph	Ph
R¹	*t*-Bu	Et			Ph
R²	H	Et	$(CH_2)_5$	$(CH_2CH_2)_2O$	H

Scheme 2.

Two types of aminophosphanes $RP(Cl)NR^2H$ and $RP(Cl)NR^1R^2$ (with primary and secondary amine substituents), are selectively obtained from this reaction in high yield. The use of hexane as a solvent for these transformations is essential. On one hand, a very low solubility of the ammonium salt in aliphatic solvents makes further purification of the product by distillation unnecessary. Even

traces of the ammonium salt in the resulting product are responsible for the degradation of $RP(Cl)NR^1R^2$ [20,21]. Thus, a very low impurity of the ammonium salt in the product that is achieved in the aliphatic solvent admits a long storage of the product (no decomposition after 3 months according to ^{31}P NMR spectra).



Scheme 3.

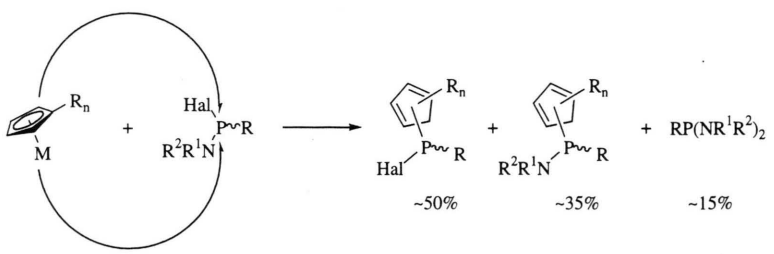
The chlorine substituent in the aminoalkylchlorophosphanes (**1a–o**) can be replaced by iodine using NaI as iodinating agent [22] to form alkyl-*N,N*-dialkylamino(iodo)phosphanes (Scheme 3). *t*-Butyl-*N,N*-diethylamino(iodo)phoshane (**1p**) has been obtained by this method in quantitative yield. The highly air- and moisture sensitive products **1a–p** were characterized by EI-MS, ^1H and ^{31}P NMR spectroscopy, and elemental analyses.

The second step of method „b" is the alkylation of the phosphorus(III) atom by organometallic derivatives of alkyl-substituted cyclopentadienes, indenes and fluorenes. These carbanions are different in structure and nucleophilicity. The first experiments have demonstrated that the reaction takes place only in THF as a solvent. In an attempt to prepare *t*-butyl-(*N,N*-diethylamino)-(tetramethylcyclopentadienyl)phosphane, tetramethylcyclopentadienyllithium (Me_4CpLi) was reacted with one equivalent of *t*-$BuP(Cl)NEt_2$ (**1b**) in THF at −78 °C. The reaction resulted in an unexpected mixture of products (Scheme 4). For the sake of a better understanding different cyclopentadienides were applied in the reaction with different precursors **1a–p**. The reactions of R_nCpLi, R_nCpNa, R_nCpK and $(R_nCp)_2Mg$ with **1a–p** lead to a mixture with similar ratios of products, according to ^{31}P and ^1H NMR data (Scheme 4).

From the formal point of view, Cp-salts react with compounds **1a–p** in two different ways, *i.e.* via a formal nucleophilic substitution reaction at P–Cl and P–N bonds. The ratio of the products does not depend on the nature of the metal cation, the solvent, and the type of the halogen substituent (Cl or I). It is worth to note that CpTl and $Me_4CpSnMe_3$ do not react with alkyl(aryl)chloro-*N,N*-dialkylaminophosphanes at all.

It appears that the formation of the target product $R_nCp(R)PNR^1R^2$ proceeds slowly, while an excess of the starting $RP(Hal)NR^1R^2$ is still present in the reaction mixture. In this case $RP(Hal)NR^1R^2$ may react with the product $R_nCp(R)PNR^1R^2$ leading to $R_nCp(R)PHal$ and $RP(NR^1R^2)_2$, respectively.

The reactivity of alkyldiaminophosphanes $RP(NR^1R^2)_2$ with cleavage of the P–N bond in the presence of R^3MgBr has been described and used for the synthesis of alkylphosphanes $RP(R^3)NR^1R^2$ (R^3 = Me) [23]. In order to exclude the possibility that mono-Cp-organometallics can react with alkylaminochlorophosphanes in the same manner, an investigation of the reaction of R_nCpM or $R_nCpM{\times}L$ (M = Li; L = TMEDA or crown-4) with $MeP(NEt_2)_2$ was performed under different conditions. The reaction was monitored by ^{31}P NMR spectroscopy. It does not proceed over one week upon stirring of the reaction mixture at room temperature or even over one week at reflux in THF. In all cases the starting materials could be recovered unchanged. This fact demonstrates that the proposed interpretation is proba-

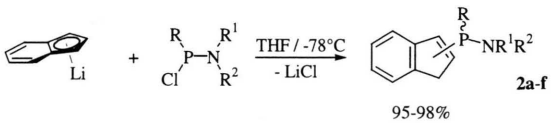


M = Li, Li×TMEDA, Li×crown-4, Na, K, Mg; R_nCp = Cp, *t*-BuCp, Me_4Cp, Cp^*; Hal = Cl, I.

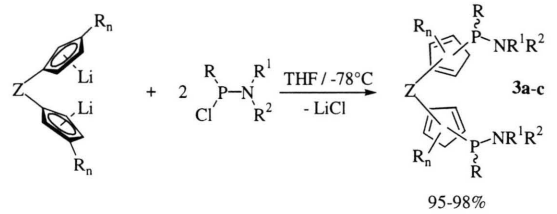
Scheme 4.

bly correct, although a detailed study of the mechanism would be necessary. We speculate that the mechanism of this kind of ligand redistribution is similar to the well known exchange reaction for the derivatives of tin [24], arsenic, antimony, and bismuth [25–28].

Surprisingly, the reactions of alkyl(aryl)aminochlorophosphanes with indenyl, fluorenyl, biscyclopentadienyl or bis-indenyl lithium/dilithium salts lead to the target compounds **2a–f** and **3a–c** in high yields (Scheme 5).



2	a	b	c	d	e	f
R	*t*-Bu	Me	*t*-Bu	*t*-Bu	Me	*t*-Bu
R¹	Et	Et	*t*-Bu	Et	Et	*t*-Bu
R²	Et	Et	H	Et	Et	H
R_nCp	Ind	Ind	Ind	Flu	Flu	Flu



3	a	b	c
R	*t*-Bu	*t*-Bu	*t*-Bu
R¹	Et	Et	Et
R²	Et	Et	Et
$(R_nCp)_2Z$	Cp_2CMe_2	$(Ind)_2(CH_2)_2$	$(Ind)_2CEt_2$

Scheme 5.

Bis(aminocyclopentadienyl)phosphanes **3a–c** could not be prepared by method "a" as a synthetic strategy [29], and this result may be attributed to the allylic structure of the bis(alkylchlorocyclopentadienyl)phosphanes and/or the high sterical hindrance in these encumbered substrates. The addition of amines (*e.g.* Me_2NH, Et_2NH, *t*-$BuNH_2$, *i*-Pr_2NH) leads to the formation of phosphafulvene intermediates *via* β-"HCl"-elimination and to further oligomerization of these very reactive species.

All compounds synthesized are highly soluble in aliphatic solvents and exist as a mixture of isomers. The structure of Flu(*t*-Bu)PN(H)*t*-Bu (**2f**) was determined by an X-ray analysis (Fig. 1).

The geometry at the phosphorus atom can be best described as a distorted tetrahedron with the bond angles ranging from 101° to 106° [N(1)–P(1)–C(11)], which indicates a certain sterical strain in the molecule. The P(1)–N(1) bond of 1.680(2) Å and the bond P(1)–C(11) of 1.923(2) Å are somewhat longer than the typical P(III)–N and P(III)–C bond distances in most substituted organophosphorus compounds [30], which again confirms the steric hindrance in **2f**. All other structural fragments do not reveal any peculiarities.

Compounds **3a–c** have been characterized by ^1H, ^{13}C, ^{31}P NMR spectroscopy and elemental analyses. The substances possess four stereogenic centers and exist as a complex mixture of stereoisomers. Eight diastereomers are theoretically possible, some of them happen to have the same chemical shifts, and only four (three enantiomeric pairs and one *meso*-form) can be destinguished by ^{31}P NMR. The proposed number of stereoisomers

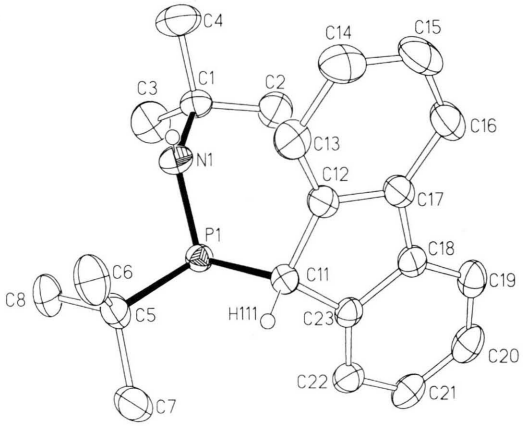


Fig. 1. ORTEP diagram of the molecule of Flu(*t*-Bu)PN(H)*t*-Bu (**2f**). Selected bond distances (Å): P(1)–N(1) = 1.680(2), P(1)–C(5) = 1.865(2), P(1)–C(11) = 1.923(2), C(11)–C(12) = 1.504(3), C(11)–C(23) = 1.509(3); Selected bond angles [°]: N(1)–P(1)–C(5) = 101.5(1), N(1)–P(1)–C(11) = 105.94(9), C(5)–P(1)–C(11) = 101.13(9), C(12)–C(11)–C(23) = 102.5(2), C(12)–C(11)–P(1) = 116.0(1), C(23)–C(11)–P(1) = 108.9(1).

is seen for 2,2-bis[(*t*-butyl-*N,N*-dialkylaminophosphanyl)indenyl]pentane (**3c**) (Fig. 2).

The ^{31}P NMR spectra confirm this assumption and show seven resonances. The *meso*-form has two phosphorus atoms that are equivalent and give rise to only one resonance. Each molecule of the *rac*-form has two nonequivalent phosphorus atoms that give two signals in the ^{31}P NMR spectrum. A total of seven resonances are observed, having different integral intensities. For the reason of complexity of the isomeric mixtures we were not able to make a detailed analysis of the proton and carbon NMR spectra. In the case of the bis(cyclopentadienyl) compound **3a** the ^{1}H and ^{13}C spectra are even more complex and the structure is proposed solely on the basis of C, H, N analysis and ^{31}P NMR spectra.

Conclusions

We have developed a new facile route to a class of P-functionalized phosphano-substituted cyclopentadienes, indenes and fluorenes and their bis(cyclopentadienyl) analogues **2a–f** and **3a–c**. A straightforward procedure to *N*-alkyl(aryl)-aminoalkyl(aryl)halogenophosphanes **1a–o** has been developed. This type of ligands are interesting with respect to application in transition metal chemistry; this work is under way.

Experimental

All manipulations involving air- and moisture sensitive materials were carried out by standard Schlenk techniques under an atmosphere of dry argon. Solvents were dried and distilled prior to use and stored under an inert atmosphere. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C on Bruker AC250P, Bruker ARX300 and Varian VXR-400 spectrometers. Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron impact with an ionization energy of 70 eV; all assignments were made with reference to the most abundant isotopes. C, H and N elemental analyses were carried out by the Microanalytical Division of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. $CpCMe_2Cp$ [31], $IndCEt_2Ind$ [32], $IndCH_2CH_2Ind$ [33], *t*-$BuPCl_2$ [34] were prepared according to the literature methods. *t*-$BuPCl_2$ has been used as a 1.02 M solution in hexane. Li, Na and K salts of the cyclopentadienyl ligand precursors and of indene and fluorene were

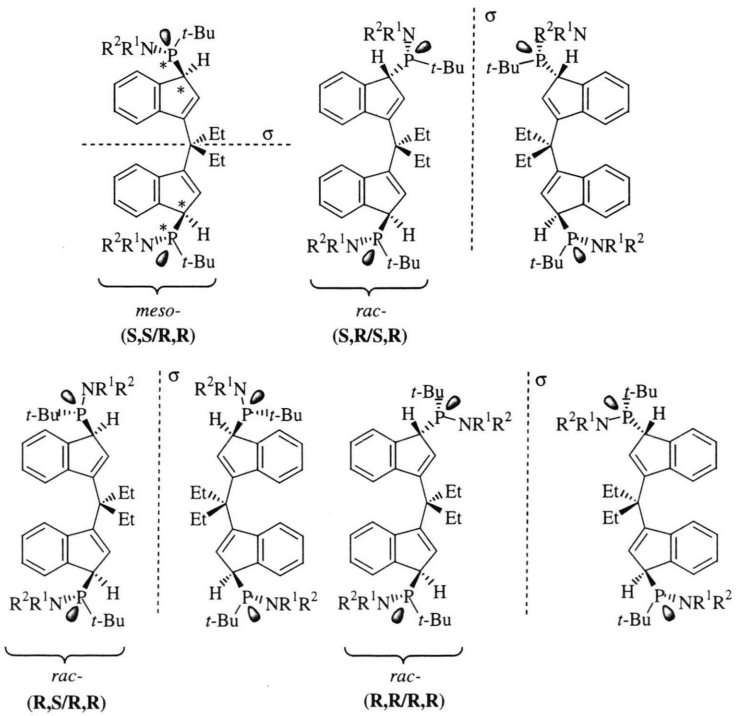


Fig. 2.

obtained by deprotonation with a 1.6 M solution of *n*-BuLi (purchased from Merck), NaH (Merck) or $PhCH_2K$ [35] by standard procedures.

General procedure for the preparation of **1a,f,k**

The total amount of the amine H_2NR^2 (2 mol; R^2 = *t*-Bu, Ph) was added at once to a solution of $RPCl_2$ (1 mol) in hexane at −100 °C (in the case of R = *t*-Bu, at room temperature), and the mixture was stirred for 5 h, while warming to room temperature (R = *t*-Bu for 24 h). Then the precipitated ammonium salt was removed by filtration. The filtrate was concentrated in vacuum (3 Torr) at room temperature to yield the product as an oily colorless liquid or as a white solid. The yields were in all cases nearly quantitative.

General procedure for the preparation of **1b,c,e,g,h,i,j,l,m,n,o**

A solution of HNR^1R^2 (2 mol) in hexane (amine/hexane = 1/30) was slowly added to a solution of $RPCl_2$ (1 mol) in hexane at −100 °C (in the case of R = *t*-Bu, at room temperature) and the mixture was stirred for 5 h, while warming to room temperature (R = *t*-Bu for 24 h). Then the precipitated ammonium salts were removed by filtration. The transparent colorless solutions were concentrated in vacuum (3 Torr) at room temperature to yield the products as oily colorless liquids or white solids. The yields were in all cases nearly quantitative.

General procedure for the preparation of **2a–f** *and* **3a–c**

The total amount of an *N,N*-dialkylaminoalkyl(-halogeno)phosphane (1 mol) was added at once to a solution/suspension of the alkali metal cyclopentadienide (1 mol) in THF at −78 °C, and the mixture was stirred for 24 h, while warming to room temperature The red or light-red solution was concentrated in vacuum. A product was extracted with a mixture of Et_2O/hexane (20/80), and the precipitated LiCl was removed by filtration. The solution obtained was concentrated in vacuum at room temperature to yield the product as an oily liquid or as a colored solid. Yield: 95–98%.

N-t-Butylamino-t-butyl-chlorophosphane (**1a**)

Obtained from 30.05 ml of *t*-$BuPCl_2$ (30.6 mmol) and 6.48 ml of *t*-$BuNH_2$ (61.3 mmol).

^{1}H NMR (400 MHz, C_6D_6): δ = 2.7 (broad s, 1 H, –NH), 1.09 (d, 9 H, *t*-BuN-, $^4J(^{31}P-^1H)$ = 0.8 Hz), 1.01 (d, 9 H, *t*-BuPCl–, $^3J(^{31}P-^1H)$ = 13.6 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 137.5. – MS (EI,70 eV): *m/z* (%) = 196 (56) [M^+]. – $C_8H_{19}ClNP$ (195.67): calcd. C 49.11, H 9.79, N 7.16; found C 48.98, H 9.67, N 7.22.

t-Butyl-chloro-N,N-diethylaminophosphane (**1b**)

Obtained from 6.15 ml of *t*-$BuPCl_2$ (6.28 mmol) and 1.33 ml of Et_2NH (12.5 mmol).

^{1}H NMR (400 MHz, C_6D_6): δ = 2.9 (m, 4 H, $-NCH_2CH_3$), 1.09 (d, 9 H, *t*-BuPCl–, $^3J(^{31}P-^1H)$ = 14.4 Hz), 0.87 (t, 6 H, $-NCH_2CH_3$, $^3J(^1H-^1H)$ = 12.0 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 158.0. – MS (EI 70, eV): *m/z* (%) = 167 (14) [M^+-CH_2CH_2]. – $C_8H_{19}ClNP$ (195.67): calcd. C 49.11, H 9.79, N 7.16; found C 49.00, H 9.67, N 7.03.

t-Butyl-chloro-N-piperidylphosphane (**1c**)

Obtained from 6.15 ml of *t*-$BuPCl_2$ (6.28 mmol) and 1.22 ml of piperidine (12.5 mmol).

^{1}H NMR (400 MHz, C_6D_6): δ = 2.93 (m, 4 H, $-N(CH_2)_2(CH_2)_3$), 1.25 (broad s, 6 H, $-N(CH_2)_2(CH_2)_3$), 1.08 (d, 9 H, *t*-BuPCl–, $^3J(^{13}P-^1H)$ = 14.4 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 155.1. – MS (EI, 70 eV) *m/z* (%) = 150 (1) [M^+–*t*-Bu]. – $C_9H_{19}ClNP$ (207.68): calcd. C 52.05, H 9.22, N 6.74; found C 52.18, H 9.13, N 6.81.

t-Butyl-chloro-N-morpholinyl-phosphane (**1d**)

Obtained from 6.15 ml of *t*-$BuPCl_2$ (6.28 mmol) and 1.1 ml of morpholine (12.5 mmol).

^{1}H NMR (400 MHz, C_6D_6): δ = 3.32 (m, 4 H, $-NCH_2CH_2O$), 2.86 (m, 4 H, $-NCH_2CH_2O$), 1.05 (d, 9 H, *t*-BuPCl–, $^3J(^{13}P-^1H)$ = 14.4 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 154.2. – MS (EI, 70 eV): *m/z* (%) = 152 (8) [M^+–*t*-Bu]. – $C_8H_{17}ClNOP$ (209.07): calcd. C 45.83, H 8.17, N 6.68; found C 45.70, H 8.03, N 6.77.

t-Butyl-chloro-phenylaminophosphane (**1e**)

Obtained from 6.15 ml of *t*-$BuPCl_2$ (6.28 mmol) and 1.14 ml of $PhNH_2$ (12.5 mmol).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.14–6.70 (m, 5 H, Ar), 3.05 (broad s, 1 H, PhN*H*–), 0.97 (d, 9 H, *t*-BuPCl-, $^3J(^{13}P-^1H)$ = 13.6 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 131.2. – MS (EI, 70 eV): *m/z* (%) = 215 (58) [M^+]. – $C_{10}H_{15}ClNP$ (215.06): calcd. C 55.69, H 7.01, N 6.49; found C 55.60, H 6.93, N 6.55.

t-Butylamino-chloro-methylphosphane (**1f**)

Obtained from 0.76 ml of $MePCl_2$ (8.55 mmol) and 1.8 ml of *t*-$BuNH_2$ (17.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 2.73 (broad s, 1 H, -NH), 1.37 (d, 3 H, CH_3PCl-, $^2J(^{31}P-^1H)$ = 10.8 Hz), 1.08 (d, 9 H, *t*-BuN–, $^4J(^{31}P-^1H)$ = 1.2 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 124.3. – MS (EI, 70 eV): *m/z* (%) = 154 (23) [M^++H]. – $C_5H_{13}ClNP$ (153.04): calcd. C 39.10, H 8.53, N 9.12; found C 39.25, H 8.41, N 9.03.

Chloro-(diethylamino)-methylphosphane (**1 g**)

Obtained from 0.76 ml of $MePCl_2$ (8.55 mmol) and 1.77 ml of Et_2NH (17.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 2.85 (m, 4 H, $-NCH_2CH_3$), 1.44 (d, 3 H, MePCl–, $^2J(^{31}P-^1H)$ = 12.3 Hz), 0.85 (t, 6 H, $-NCH_2CH_3$, $^3J(^1H-^1H)$ = 7.1 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 145.4. – MS (EI, 70 eV): *m/z* (%) = 153 (8) [M^+]. – $C_5H_{13}ClNP$ (153.04): calcd. C 39.10, H 8.53, N 9.12; found C 39.22, H 8.41, N 9.25.

Chloro-methyl-piperidylphosphane (**1h**)

Obtained from 0.76 ml of $MePCl_2$ (8.55 mmol) and 1.67 ml of piperidine (17.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 3.83 (broad s, 4 H, $-N(CH_2)_2(CH_2)_3$), 1.43 (d, 3 H, MePCl–, $^2J(^{13}P-^1H)$ = 12.7 Hz), 1.24 (broad s, 6 H, $-N(CH_2)_2(CH_2)_3$). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 141.3. – MS (EI, 70 eV): *m/z* (%) = 165 (86) [M^+]. – $C_6H_{13}ClNP$ (165.04): calcd. C 43.52, H 7.91, N 8.46; found C 43.41, H 7.83, N 8.58.

Chloro-methyl-(N-morpholinyl)phosphane (**1i**)

Obtained from 0.76 ml of $MePCl_2$ (8.55 mmol) and 1.49 ml of morpholine (17.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 3.3 (m, 4 H, $-NCH_2CH_2O$), 2.73 (m, 4 H, $-NCH_2CH_2O$), 1.34 (d, 3 H, MePCl–, $^2J(^{13}P-^1H)$ = 11.9 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 142.0. – MS (EI, 70 eV): *m/z* (%) = 167 (70) [M^+]. – $C_5H_{11}ClNOP$ (167.02): calcd. C 35.84, H 6.62, N 8.36; found C 35.71, H 6.54, N 8.23.

Chloro-methyl-(phenylamino)phosphane (**1j**)

Obtained from 0.76 ml of $MePCl_2$ (8.55 mmol) and 1.56 ml of $PhNH_2$ (17.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 7.05 (m, 2 H, Ar), 6.9 (m, 2 H, Ar), 6.8 (m, 1 H, Ar), 4.45 (broad s, 1 H, PhN*H*–), 1.25 (d, 9 H, *t*-BuPCl–, $^2J(^{13}P-^1H)$ = 11.3 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 118.5. – MS (EI, 70 eV): *m/z* (%) = 173 (5) [M^+]. – C_7H_9ClNP (173.01): calcd. C 48.44, H 5.23, N 8.07; found C 48.55, H 5.13, N 7.96.

t-Butylamino-chloro-phenylphosphane (**1k**)

Obtained from 0.75 ml of $PhPCl_2$ (5.58 mmol) and 1.18 ml of *t*-$BuNH_2$ (11.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 7.71 (m, 2 H, Ar), 7.15 (m, 3 H, Ar), 3.0 (d, 1 H, -NH, $^2J(^{31}P-^1H)$ = 13.6 Hz), 1.13 (d, 9 H, *t*-BuN–, $^4J(^{31}P-^1H)$ = 1.1 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 117.1. – MS (EI, 70 eV): *m/z* (%) = 216 (93) [M^++H]. – $C_{10}H_{15}ClNP$ (215.06): calcd. C 55.69, H 7.01, N 6.49; found C 55.78, H 6.90, N 6.38.

Chloro-(diethylamino)-phenylphosphane (**1l**)

Obtained from 0.75 ml of $PhPCl_2$ (5.58 mmol) and 1.15 ml of Et_2NH (11.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 7.69 (m, 2 H, Ar), 7.14 (m, 2 H, Ar), 7.08 (m, 1 H, Ar), 2.87 (m, 4 H, $-NCH_2CH_3$), 0.83 (t, 6 H, $-NCH_2CH_3$, $^3J(^1H-^1H)$ = 7.1 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 140.3. – MS (EI, 70 eV): *m/z* (%) = 216 (13) [M^++H]. – $C_{10}H_{15}ClNP$ (215.06): calcd. C 55.69, H 7.01, N 6.49; found C 55.76, H 6.88, N 6.34.

Chloro-piperidyl-phenylphosphane (**1 m**)

Obtained from 0.75 ml of $PhPCl_2$ (5.58 mmol) and 1.15 ml of piperidine (11.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 7.68 (m, 2 H, Ar), 7.3–7.0 (m, 3 H, Ar), 2.85 (m, 4 H, $-N(CH_2)_2(CH_2)_3$), 1.2 (m, 6 H, $-N(CH_2)_2(CH_2)_3$). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 138.9. – MS (EI, 70 eV): m/z (%) = 227 (20) [M^+]. – $C_{11}H_{15}ClNP$ (227.06): calcd. C 58.03, H 6.64, N 6.15; found C 57.89, H 6.71, N 6.28.

Chloro-(N-morpholinyl)-phenylphosphane (**1n**)

Obtained from 0.75 ml of $PhPCl_2$ (5.58 mmol) and 0.97 ml of morpholine (11.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 7.65 (m, 2 H, Ar), 7.14 (m, 2 H, Ar), 7.09 (m, 1 H, Ar), 3.27 (m, 4 H, $-NCH_2CH_2O$), 2.75 (m, 4 H, $-NCH_2CH_2O$). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 136.9. – MS (EI, 70 eV): *m/z* (%) = 229 (54) [M^+]. – $C_{10}H_{13}ClNOP$ (229.04): calcd. C 52.30, H 5.71, N 6.10; found C 52.21, H 5.82, N 5.97.

Chloro-phenylamino-phenylphosphane (**1o**)

Obtained from 0.75 ml of $PhPCl_2$ (5.58 mmol) and 0.5 ml of $PhNH_2$ (11.1 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 7.56 (m, 2 H, Ar), 7.2–6.7 (m, 8 H, Ar and PhN), 4.82 (d, 1 H,

PhN*H*–, $^2J(^{13}P-^1H)$ = 25.0 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 109.1. – MS (EI, 70 eV): m/z (%) = 235 (2) [M^+], 200 (33) [M^+-Cl]. – $C_{12}H_{11}ClNP$ (235.03): calcd. C 61.16, H 4.70, N 5.94; found C 60.01, H 4.64, N 5.83.

t-Butyl-diethylamino-iodophosphane (**1p**)

To a solution of 2.2 g *t*-BuP(Cl)NEt_2 (**1b**) (10.22 mmol) was added 2 g of NaI (>10 mmol). Then the reaction mixture was refluxed for 5 h. The solids were removed by filtration. A transparent yellow solution was concentrated in vacuum (3 Torr) at room temperature to yield the product as an oily yellow liquid in quantitative yield.

^1H NMR (300 MHz, C_6D_6): δ = 2.85 (m, 4 H, $-NCH_2CH_3$), 1.13 (d, 9 H, *t*-BuPCl–, $^3J(^{31}P-^1H)$ = 14.4 Hz), 0.87 (t, 6 H, $-NCH_2CH_3$, $^3J(^1H-^1H)$ = 7.2 Hz). – $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 48.1 (d, $-NCH_2CH_3$, $^2J(^{31}P-^{13}C)$ = 12.0 Hz), 35.8 (d, C_q, *t*-Bu, $^1J(^{31}P-^{13}C)$ = 42.0 Hz), 27.1 (d, C_{Me}, *t*-Bu, $^2J(^{31}P-^{13}C)$ = 19.3 Hz), 12.6 (d, $-NCH_2CH_3$, $^3J(^{31}P-^{13}C)$ = 5.1 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C): δ = 174.0. – MS (EI, 70 eV): *m/z* (%) = 271 (2) [M^+-CH_3+H], 216 (5) [M^+-Et_2N], 162 (11) [*t*-BuP(H)NEt_2]. – $C_8H_{19}INP$ (287.12): calcd. C 33.47, H 6.67, N 4.88; found C 33.58, H 6.53, N 5.04.

t-Butyl-diethylamino(1H-inden-1-yl)phosphane (**2a**)

Obtained from of 0.49 g IndLi (4.01 mmol) and 0.78 g of *t*-BuP(Cl)NEt_2 (**1b**) (4.01 mmol).

IR (film): ν = 3000, 2950, 2875, 2864, 2396, 1558, 1457, 1180, 1093, 874, 773, 736 (P–N), 415. – ^1H NMR (300 MHz, C_6D_6): δ = 7.80 (m, 1 H, Ar), 7.23–7.18 (m, 1 H, Ar), 7.12 (m, 2 H, Ar), 6.43 (m, 1 H, Vin), 3.1–3.0 (m, 2 H, All), 2.93 (m, 4 H, $-NCH_2CH_3$), 1.19 (d, 9 H, *t*-Bu, $^3J(^{31}P-^1H)$ = 12.9 Hz), 0.83 (t, 6 H, $-NCH_2CH_3$, $^3J(H-H)$ = 5.4 Hz). – $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 148.0 (d, C_q, Ar, Ind, $^2J(^{31}P-^{13}C)$ = 23.6 Hz), 143.4 (C_q, Ar, Ind), 142.3 (d, C_q, Vin, Ind, $^1J(^{31}P-^{13}C)$ = 25.5 Hz), 136.6 (CH, Vin, Ind), 126.4 (CH, Ar, Ind), 124.9 (CH, Ar, Ind), 123.6 (CH, Ar, Ind), 121.0 (d, CH, Ar, Ind, $^3J(^{31}P-^{13}C)$ = 7.4 Hz), 46.5 (d, NCH_2CH_3, $^2J(^{31}P-^{13}C)$ = 15.7 Hz), 40.2 (C, All, Ind), 33.6 (d, C_q, *t*-Bu, $^1J(^{31}P-^{13}C)$ = 17.6 Hz), 28.1 (d, *t*-Bu, $^2J(^{31}P-^{13}C)$ = 16.1 Hz), 15.1 (d, $-NCH_2CH_3$, $^3J(^{31}P-^{13}C)$ = 3.2 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 63.9. – MS (EI, 70 eV): *m/z* (%) = 275 (7) [M^+], 218 (76) [M^+-t-Bu], 160 (27) [*t*-BuPN(H)*t*-Bu]. – $C_{17}H_{28}PN$ (277.38): calcd. C 73.61, H 10.17, N 5.05; found C 73.52, H 10.27, N 4.91.

Diethylamino(1H-inden-3-yl)methylphosphane (**2b**)

Obtained from 2.0 g of IndLi (16.4 mmol) and 2.51 g of MeP(Cl)NEt_2 (**1 g**) (16.4 mmol).

^1H NMR (400 MHz, C_6D_6): δ = 7.81 (m, 1 H, Av) 7.36 (m, 1 H, Ar), 7.28–7.24 (m, 2 H, Ar), 6.95–6.91 (m, 1 H, Ar), 3.25 (m, 2 H, All, Ind), 2.8 (m, 4 H, $-NCH_2CH_3$), 1.08 (d, 3 H, MeP-, $^2J(^{31}P-^1H)$ = 9.8 Hz), 0.83 (t, 6 H, $-NCH_2CH_3$, $^3J(H-H)$ = 7.7 Hz). – $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 146.3 (d, C_q, Ar, Ind, $^3J(^{31}P-^{13}C)$ = 4.3 Hz), 141.4 (d, C_q, Ar, Ind, $J(^{31}P-^{13}C)$ = 28.5 Hz), 137.5 (d, CH, Vin, Ind, $^2J(^{31}P-^{13}C)$ = 7.2 Hz), 137.5 (d, CH, Vin, Ind, $^2J(^{31}P-^{13}C)$ = 10.1 Hz), 126.8 (CH, Ar, Ind), 126.5 (CH, Ar, Ind), 125.4 (CH, Ar, Ind), 123.9 (CH, Ar, Ind), 43.6 (d, NCH_2CH_3, $^2J(^{31}P-^{13}C)$ = 14.6 Hz), 39.5 (C, All, Ind), 15.3 (d, $-NCH_2CH_3$, $^3J(^{31}P-^{13}C)$ = 7.9 Hz), 11.0 (d, MeP–, $^1J(^{31}P-^{13}C)$ = 28.4 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 53.8. – MS (EI, 70 eV): *m/z* (%) = 233 (5) [M^+], 218 (80) [M^+–Me]. – $C_{14}H_{20}PN$ (233.13): calcd. C 72.08, H 8.64, N 6.00; found C 72.22, H 8.78, N 5.89.

t-Butylamino-t-butyl(1H-inden-3-yl)phosphane (**2c**)

Obtained from 0.79 g of IndLi (6.50 mmol) and 1.27 g of *t*-BuP(Cl)NH(*t*-Bu) (**1a**) (6.5 mmol).

IR (film): ν = 3000, 2961, 2771, 2380, 1635, 1578, 1540, 1192, 1180, 953, 736 (P–N), 656. – ^1H NMR (300 MHz, C_6D_6): δ = 7.80 (d, 1 H, Ar), 7.24 (d, 1 H, Ar), 7.18–7.12 (dt, 2 H, Ar), 6.22 (m, 1 H, Vin), 3.07 (m, 2 H, All), 1.68 (d, 1 H, –NH, $^2J(^{31}P-^1H)$ = 11.9 Hz), 1.15 (s, 9 H, *t*-BuN), 1.05 (d, 9 H, *t*-BuP, $^3J(^{31}P-^1H)$ = 12.8 Hz). – $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 147.7 (d, C_q, Ind, $J(^{31}P-^{13}C)$ = 23.6 Hz), 147.4 (d, C_q, Ind, $J(^{31}P-^{13}C)$ = 32.4 Hz), 144.6 (C_q, Ar, Ind), 141.1 (CH, Vin, Ind), 126.3 (CH, Ar, Ind), 125.0 (CH, Ar, Ind), 123.8 (CH, Ar, Ind), 122.4 (d, CH, Ar, Ind, $^3J(^{31}P-^{13}C)$ = 6.2 Hz), 50.7 (d, C_q, *t*-BuN, $^2J(^{31}P-^{13}C)$ = 17.2 Hz), 39.4 (d, C, All, Ind, $^3J(^{31}P-^{13}C)$ = 2.8 Hz), 32.1 (d, *t*-BuN, $^3J(^{31}P-^{13}C)$ = 8.3 Hz), 27.4 (d, C_q, *t*-BuP, $^1J(^{31}P-^{13}C)$ = 16.4 Hz), 26.6 (d, *t*-BuP, $^2J(^{31}P-^{13}C)$ = 15.0 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 21.7. – MS (EI, 70 eV): *m/z* (%) = 275 (9) [M^+], 218 (65) [M^+-t-Bu], 162 (100) [M-2–*t*-Bu]. – $C_{17}H_{28}PN$ (277.38): calcd. C 73.61, H 10.17, N 5.05; found C 73.69, H 10.01, N 4.87.

t-Butyl-diethylamino(9-fluorenyl)phosphane (**2d**)

Obtained from 2.0 g of FluLi (11.61 mmol) and 2.26 g of *t*-BuP(Cl)NEt_2 (**1b**) (11.61 mmol).

^{1}H NMR (200 MHz, C_6D_6): δ = 7.8–7.7 (m, 1 H), 7.68–7.60 (m, 1 H), 7.57–7.52 (m, 2 H), 7.20–6.97 (m, 4 H), 4.2 (d, 1 H, $^2J(^{31}P-^1H)$ = 6.2 Hz), 2.68–2.34 (m, 4 H, 2 $-NCH_2CH_3$), 1.09 (d, 9 H, *t*-Bu, $^3J(^{31}P-^1H)$ = 13.0 Hz), 0.43 (t, 6 H, 2 $-NCH_2CH_3$, ^3J(H–H) = 7.0 Hz). – $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ = 145.8 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 10.3 Hz), 145.1 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 2.1 Hz), 140.7 (C_q, Flu), 140.2 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 2.5 Hz), 125.6 (d, CH, Flu $J(^{31}P-^{13}C)$ = 4.5 Hz), 125.5 (CH, Flu), 125.3 (CH, Flu), 125.1 (CH, Flu), 124.7 (CH, Flu), 123.9 (CH, Flu), 118.9 (CH, Flu), 118.4 (CH, Flu), 49.5 (C, All, Flu, $^1J(^{31}P-^{13}C)$ = 45.3 Hz), 45.2 (d, $-NCH_2CH_3$, $^2J(^{31}P-^{13}C)$ = 16.1 Hz), 34.1 (d, C_q, *t*-Bu, $^1J(^{31}P-^{13}C)$ = 26.8 Hz), 27.8 (d, *t*-Bu, $^2J(^{31}P-^{13}C)$ = 18.2 Hz), 13.5 (d, $-NCH_2CH_3$, $^3J(^{31}P-^{13}C)$ = 2.1 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 63.3. – MS (EI, 70 eV): *m/z* (%) = 277 (3) [M^+], 253 (35) [M^+-NEt_2], 165 (100) [Flu]. – $C_{21}H_{28}PN$ (325.43): calcd. C 77.51, H 8.67, N 4.30; found C 77.39, H 8.51, N 4.23.

Diethylamino(9-fluorenyl)methylphosphane (**2e**)

Obtained from 8.1 g of FluLi (47.06 mmol) and 7.22 g of MeP(Cl)NEt_2 (**1 g**) (47.06 mmol).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.68 (m, 1 H, Vin, Flu), 7.58 (d, 1 H, Vin, Flu), 7.23 (d, 1 H, Vin, Flu), 7.23 (m, 4 H, Vin, Flu), 4.02 (d, 1 H, All, Flu, $^2J(^{31}P-^1H)$ = 6.5 Hz), 2.6 (m, 4 H, $-NCH_2CH_3$), 1.22 (d, 3 H, MeP, $^2J(^{31}P-^1H)$ = 8.4 Hz), 0.68 (t, 6 H, $-NCH_2CH_3$, $^3J(^1H-^1H)$ = 7.1 Hz). – $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 145.4 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 3.8 Hz), 144.8 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 7.9 Hz), 141.9 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 2.2 Hz), 141.2 (C_q, Flu), 126.7 (CH, Flu), 126.5 (CH, Flu), 126.3 (CH, Flu), 125.5 (CH, Flu, $J(^{31}P-^{13}C)$ = 6.02 Hz), 125.3 (CH, Flu, $J(^{31}P-^{13}C)$ = 3.7), 120.4 (CH, Flu), 120.1 (CH, Flu), 53.6 (d, C, All, Flu, $^1J(^{31}P-^{13}C)$ = 34.5 Hz), 44.2 (d, $-NCH_2CH_3$, $^2J(^{31}P-^{13}C)$ = 14.9 Hz), 15.2 (d, $-NCH_2CH_3$, $^3J(^{31}P-^{13}C)$ = 3.1 Hz), 13.4 (d, MeP–, $^1J(^{31}P-^{13}C)$ = 21.0 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 59.4. – MS (EI, 70 eV): *m/z* (%) = 212 (28) [M^+-NEt_2]. – $C_{18}H_{22}PN$ (283.14): calcd. C 76.30, H 7.83, N 4.94; found C 76.45, H 7.71, N 4.84.

t-Butylamino-t-butyl(9-fluorenyl)phosphane (**2f**)

Obtained from 1.79 g of FluLi (5.8 mmol) and 1.13 g of *t*-BuP(Cl)NH(*t*-Bu) (**1a**)(5.8 mmol).

^{1}H NMR (200 MHz, C_6D_6): δ = 7.53–749 (m, 2 H), 7.27–7.23 (m, 1 H), 7.15–7.08 (m, 5 H), 3.84 (s, 1 H, All), 1.56 (d, 1 H, –NH, $^2J(^{31}P-^1H)$ = 10.3 Hz), 0.89 (d, 9 H, *t*-BuP, $^3J(^{31}P-^1H)$ = 12.5 Hz), 0.58 (s, 9 H, *t*-BuN). – $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ = 147.0 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 15.1 Hz), 142.3 (C_q, Flu), 140.8 (C_q, Flu), 139.1 (d, C_q, Flu, $J(^{31}P-^{13}C)$ = 3.3 Hz), 125.7 (CH, Flu), 125.1 (CH, Flu), 124.9 (CH, Flu), 124.3 (CH, Flu), 124.1 (CH, Flu), 124.1 (CH, Flu), 119.1 (CH, Flu), 118.5 (CH, Flu), 48.6 (d, C_q, *t*-BuN, $^2J(^{31}P-^{13}C)$ = 18.2 Hz), 47.3 (d, C_q, All, Flu, $^1J(^{31}P-^{13}C)$ = 39.2 Hz), 30.4 (d, *t*-BuN, $^3J(^{31}P-^{13}C)$ = 7.8 Hz), 30.0 (d, C_q, *t*-BuP, $^1J(^{31}P-^{13}C)$ = 13.6 Hz), 25.8 (d, *t*-BuP, $^2J(^{31}P-^{13}C)$ = 16.5 Hz). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 49.5; – MS (EI, 70 eV): *m/z* (%) = 325 (1) [M^+], 268 (5) [M^+-t-Bu], 212 (12) [M-2–*t*-Bu], 165 (36) [Flu], 160 (100) [*t*-BuPNH–*t*-Bu]. – $C_{21}H_{28}PN$ (325.43): calcd. C 77.51, H 8.67, N 4.31; found C 77.40, H 8.57, N 4.25.

2,2-Bis[(t-butyl-diethylaminophosphanyl)cyclopentadienyl]propane (**3a**)

Obtained from 1.6 g of $[Cp_2CMe_2]Li_2$ (4.76 mmol) and 1.86 g of *t*-BuP(Cl)NEt_2 (**1b**) (4.76 mmol).

Mixture of isomers: – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 74.6, 74.0, 73.9, 73.8, 73.8, 73.5, 73.5, 73.3, 73.2, 73.0, 73.0, 72.9, 70.4. – $C_{29}H_{52}P_2N_2$ (490.69): calcd. C 70.99, H 10.68, N 5.91; found C 70.90, H 10.79, N 5.78.

1,2-Bis[(t-butyl-diethylaminophosphanyl)indenyl]ethane (**3b**)

Obtained from 4.1 g of $[Ind_2(CH_2)_2]Li_2$ (9.81 mmol) and 3.84 g of *t*-BuP(Cl)NEt_2 (**1b**) (19.62 mmol).

Mixture of isomers: – ^{1}H NMR (400 MHz, C_6D_6): δ = 7.9–7.2 (several m, 4 H, Ar, Ind), 6.8–6.0 (several m, 1 H, Vin, Ind), 4.2–3.7 (several m, 1 H, All, Ind), 3.2–2.7 (several m, 6 H, $-NCH_2CH_3$ and $-CH_2CH_2$-), 1.5–0.5 (several m, *t*-BuP and $-NCH_2CH_3$). – $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 144.0–141.0 (several d, C_q, $J(^{31}P-^{13}C)$ = 3.8 Hz), 131.1–131.0 (d, C_q, Ind, $J(^{31}P-^{13}C)$ = 6.1 Hz), 126.4–124.0 (several d, CH, Ind), 68.0 (C, All, Ind), 51.0–48.0 (two d, C_q, *t*-BuP–), 38.0 ($-CH_2CH_2-$), 34.6 (a number of resonance, $-NCH_2CH_3$), 28.9 (several d, CH_3, *t*-BuP–), 15.0 ($-NCH_2CH_3$). – $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 91.7, 91.6, 91.6, 91.5, 86.8, 86.7, 86.6, 86.6. – MS (EI, 70 eV): *m/z* (%) = 448 (1) [M^+-t-Bu–NEt_2+H], 160 (95) [*t*-BuPNEt_2], 128 (86) [*t*-BuPNEt_2-2CH_4], 104 (100) [HPNEt_2], 74 (43) [H_2NEt_2], 57 (26) [*t*-Bu]. – $C_{36}H_{58}P_2N_2$

(580.81): calcd. C 74.45, H 10.07, N 4.82; found C 74.39, H 10.13, N 4.71.

2,2-Bis[(t-butyl-diethylaminophosphanyl)indenyl]-pentane (**3c**)

Obtained from 4.72 g of $[Ind_2CEt_2]Li_2$ (10.24 mmol)and 4.01 g of *t*-BuP(Cl)NEt_2 (**1b**) (20.48 mmol).

Mixture of isomers: – ^{1}H NMR (200 MHz, C_6D_6): δ = 8.0–6.8 (several m, 4 H, Ar, Ind), 6.8–6.41 (several m, 1 H, Vin, Ind), 4.36–4.30 (several m, 1 H, All, Ind), 3.5–2.21 (several m, 6 H, –N$CH_2$$CH_3$ and –C$CH_2$$CH_3$), 1.64–1.0 (several m, 12 H, *t*-BuP– and –N$CH_2$$CH_3$). – ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ = 151.0–129.0 (several m, C_q, Ind), 124.7–117.6 (several m, C_q and CH, Ind), 58.5–45.4 (two d, C_q and C, All, Ind), 29.5–29.1 (two d, CH_3), 26.5–25.0 (several m, –$CH_2$$CH_3$), 15.4 (–N$CH_2$$CH_3$), 8.4 (–$CH_2$$CH_3$). – ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 90.8, 90.6, broad m 89.0, 56.1, 55.3, 54.8; – MS (EI, 70 eV): *m/z* (%) = 286.2 (25) [$C_{18}H_{25}NP$], 160 (10) [*t*-BuPNEt_2], 115 (35) [Ind], 72 (30) [–NEt_2], 58 (100) [*t*-BuH], 29 (80) [Et]. – $C_{39}H_{60}P_2N_2$ (618.86): calcd. C 75.69, H 9.77, N 4.53; found C 75.54, H 9.90, N 4.40.

X-Ray structure determination of **2f**

Diffraction-quality crystals of **2f** were obtained by cooling an n-hexane solution. A crystal data summary is given in Table 1. A yellow specimen with dimensions of 0.45 × 0.30 × 0.25 mm^3 was mounted on the top of a glass fiber and studied on an Enraf-Nonius CAD4 four-circle diffractometer with Cu–K_α (1.54178 Å) radiation at –50 °C. The structure was solved in the space group $P2_1/n$ by direct methods and refined by full-matrix least-squares on F^2 by using the SHELX-96 program package [36]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference-Fourier maps and refined in an isotropic approximation. Further details can be obtained from the Cambridge Crystallographic Database on quoting the depository number CCDC 160960. E-mail: deposit@ccdc.cam.ac.uk.

Table 1. Crystal data and experimental details of the crystal structure determination of **2f**.

Crystal data:	
Chemical formula	$C_{21}H_{28}NP$
Formula weight	325.41 g/mol
Density (calcd)	1.132 g/cm^3
Habitus, color	prism, yellow
Crystal dimensions	0.45 × 0.30 × 0.25 mm
Crystal system	monoclinic
Space group	$P2_1/n$, Z = 4
Unit cell dimensions:	
a [Å]	9.990(2)
b [Å]/β [°]	15.298(3)/101.33(3)°
c [Å]	12.742(3)
Volume [Å^3]	1909.4(7)
F(000)	704
Abs. coeff. [mm^{-1}]	1.248
Data collection:	
Radiation	Cu–Kα (1.54178 Å), graphite monochromator
Temp. [K]	223(2)
θ-range	4.57 to 60.05°
Index ranges	$0 \geq \delta$ h δ 11, $0 \geq \delta$ k δ 17, $-14 \geq \delta$ l δ 14
Solution and refinement:	
Refl. coll./unique	3020/2838
Refl. obs. [$I > 2\ \sigma(I)$]	2450
Largest peak/hole	0.246/–0.287 e/ Å^3
Solution	direct methods
Refinement	full-matrix, F^2
Data/parameters	2838/321
wR_2, all data	0.1336
$R(F)$ [$I > 2\ \sigma(I)$]	0.0449
Goodness-of-fit on F^2	1.107

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