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Synthesis of the first representatives of amino bis(picolyl) and amino bis(quinaldinyl) phosphines

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Dedicated to Professor Peter Klüfers on the occasion of his 65th birthday

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ABSTRACT

First amino bis(picolyl) and amino bis(quinaldinyl) phosphines were synthesized by reaction of the corresponding amino dichlorophosphines – the new carbazolyl dichlorophosphine (**1**) and diisopropylamino dichlorophosphine (**2**) with either picolylTMS (**6**), quinaldinylTMS (**15**) or their respective lithium derivatives **12** and **16**. The deviation of the standard synthesis via the silyl route is necessary for the synthesis of the diisopropylamino derivatives **11** and **14** due to the fact that compound **2** is not reacting with **6** or **15** even at reflux conditions. All new compounds are extensively characterized by multinuclear NMR spectroscopy and some also by single crystal X-ray diffraction. Also the molecular and crystal structure of the new dichlorophosphine **1** was determined.

1. Introduction

PN-Ligands are due to the soft phosphorus and hard nitrogen coordination site interesting and highly desirable multidentate and hemilable ligands that show a huge variety of coordination patterns.[1] Transition metal complexes of such ligands display catalytic properties and can be potentially used for a great number of catalyzed reactions.[2] One possibility to design a molecule with this structural motive is to attach one, two[3] or three[4] picolyl (=C_5H_4N–2–CH_2-) moieties to phosphorus. The picolyl substituent, with its methylene group as a spacer between the pyridine ring and the phosphorus atom provides also geometrical flexibility for this compound as a ligand. Currently only a hand full of derivatives of bis(picolyl) phosphines are known in literature.[3] In our recent work on the synthesis and characterization of methoxyphenyl substituted bis(picolyl) phosphines we presented a detailed overview of the available bis(picolyl) phosphines and some of their metal complexes and added our own work to the existing library of derivatives.[3b] In all available bis(picolyl) phosphines, all substituents at phosphorus are attached to it by a covalent P–C bond.

Here we present the synthesis of first amino substituted bis(picolyl) and bis(quinaldinyl) phosphines starting from the new carbazolyl dichlorophosphine (**1**) and diisopropylamino dichlorophosphine (**2**). In these compounds, the aminofunctionality at phosphorus is anticipated to significantly influence the competing PN coordination of the ligands. The synthesis of the hitherto unknown carbazolyl dichlorophosphine (**1**) is also reported. All new compounds are characterized by multinuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopy and some of them also by single crystal X-ray diffraction.

2. Results and discussion

2.1. Syntheses

*2.1.1. Synthesis of the dichlorophosphines **1**–**4**.* The new carbazolyl dichlorophosphine (**1**) was synthesized applying the literature procedure for the preparation of *i*Pr_2NPCl_2 (**2**),[5] Ph_2NPCl_2 (**3**)[5] and Bn_2NPCl_2 (**4**).[6] The reaction started from carbazole, which was allowed to react with PCl_3 and TEA to form the dichlorophosphine **1** in 53% yield (Scheme 1). Dichlorophosphines **2**–**4** were prepared analogously. Dichlorophosphine **1** was isolated as a colorless to

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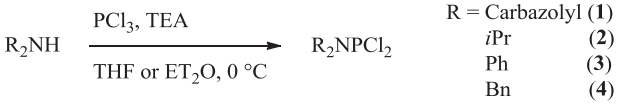
yellow crystalline solid which, due to similar solubility properties, was always accompanied by traces of the starting material carbazole. Compound **1** is highly sensitive towards humidity and it is highly soluble in polar solvents like DCM, THF and MeCN. It is sparingly soluble in Et_2O and pentane. The identity of dichlorophosphine **1** was doubtlessly confirmed by multinuclear NMR spectroscopy and single crystal X-ray diffraction. Also the crystal structure of **3** was determined. The analytical data of **2**–**4** compare well with those from the literature.[5,6]

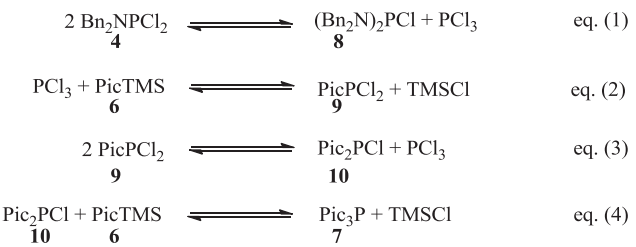


Scheme 1. Synthesis of the amino dichlorophosphines **1**–**4** starting from the corresponding secondary amines.

2.1.2. Synthesis of the amino bis(picolyl) and amino bis(quinaldinyl) phosphines. Carbazolyl bis(picolyl) phosphine (**5**) was synthesized by the reaction of the dichlorophosphine **1** with the twofold amount of PicTMS (**6**) (Pic=C_5H_4N–2–CH_2) in THF following a procedure described in the literature (Scheme 2).[3b,7] Phosphine **5** was isolated as colorless to yellowish solid by extraction of the crude product with dry Et_2O in very good yield (92%). It was highly soluble in Et_2O and other polar and aprotic solvents like THF and MeCN. Compound **5** is highly sensitive towards oxidation in air.

In contrast to the reaction of carbazolyl dichlorophosphine (**1**) with 2 equiv of PicTMS (**6**) the corresponding reaction of iPr_2NPCl_2 (**2**) and Bn_2NPCl_2 (**4**) with PicTMS (**6**) did not lead to the desired amino bis(picolyl) phosphines. Even after refluxing the reaction mixture for 20 h, amino dichlorophosphine **2** did not react with PicTMS (**6**).

The reaction of Bn_2NPCl_2 (**4**) with 2 equiv of PicTMS (**6**) under the same conditions resulted unexpectedly in the formation of tris(picolyl) phosphine (**7**). It was clearly identified in the crude reaction mixture by ^{31}P NMR spectroscopy (**7**, δ_P=−13.1, $^2J_{PH}$=1.5 Hz)[4] (eq. (4) Scheme 3). Its formation is most probably due to a dismutation of the dichlorophosphine **4**. Such dismutations have been described for dichlorophosphines and phosphines.[8] Substituent exchange between two molecules of Bn_2NPCl_2 (**4**) yields in equilibrium the chlorophosphine **8** and PCl_3. From all in the reaction mixture present chlorophosphines, PCl_3 as the most reactive one preferentially undergoes substitution with PicTMS (**6**) to give **9**. Most probably **9** undergoes similar dismutation to give **7** and again PCl_3 (Scheme 3).



Scheme 3. Dismutation reaction of Bn_2NPCl_2 (**4**) in the presence of the twofold amount of PicTMS (**6**) at reflux conditions for 20 h.

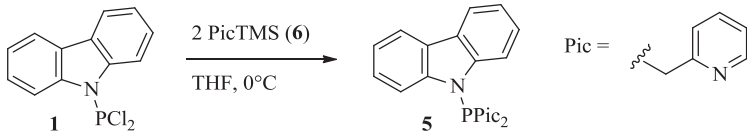
To confirm this mechanism, the formation and dismutation abilities of **9** were investigated separately. Dichlorophosphine **9** can quantitatively be synthesized according to eq. (2) Scheme 3 at −78 °C. Upon removal of the solvent (THF) at ambient temperature, almost quantitative dismutation occurs to form chlorophosphine **10** and PCl_3, which simultaneously was removed in vacuo.

The fast and easy dismutation of $PicPCl_2$ (**9**) is remarkable, as the corresponding benzyldichlorophosphine $BnPCl_2$ is a stable and distillable (at 60 °C) compound.[9] This observation underlines the special properties of the benzylic position in 2-picoline.

For the synthesis of diisopropylamino bis(picolyl) phosphine (**11**) picolyl-lithium (**12**) which was obtained by metalation of 2-picoline with *n*BuLi, was directly reacted with the dichlorophosphine **2** (Scheme 4).

The separation of the LiCl formed during the reaction was not trivial, due to the bad solubility of **11** in solvents that do not dissolve the salt (pentane, toluene). Nevertheless, we were able to isolate **11** as yellow solid by extraction with pentane (32%). Phosphine **11** is highly sensitive towards oxidation in air.

Carbazolyl bis(quinaldinyl) phosphine (**13**) and diisopropylamino bis(quinaldinyl) phosphine (**14**) were synthesized as described for the bis(picolyl) derivatives **5** and **11**, starting from the respective amino dichlorophosphine **1** or **4** and QuinaldinylTMS (**15**)[10] in the case of **1** (Scheme 5) or quinaldinyl-lithium (**16**) in the case of **4** (Scheme 6).

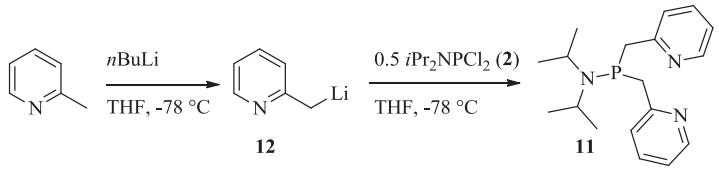


Scheme 2. Synthesis of carbazolyl bis(picolyl) phosphine (**5**) by reaction of PicTMS (**6**) with dichlorophosphine **1**.

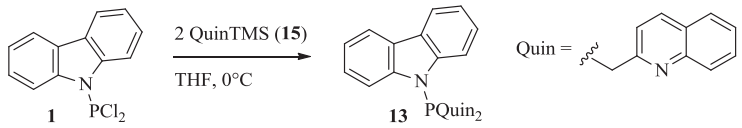
Compound **13** was isolated by removing the THF and washing of the crude reaction mixture several times with Et_2O. It was obtained as a yellowish to orange solid in very good yield (89%). Bis(quinaldinyl) phosphine **13** is highly sensitive towards oxidation in air, as is also **14**. Phosphine **14** was isolated by extraction of the crude reaction mixture with toluene in very good yield (94%) as a bright yellow crystalline solid. Phosphines **13** and **14** are soluble in Et_2O, THF, DCM, MeCN and toluene. The identity of both bis(quinaldinyl) phosphines is confirmed by ^1H, ^{13}C and ^{31}P NMR spectroscopy and in the case of **14**, also by single crystal X-ray diffraction.

2.2. Characterization

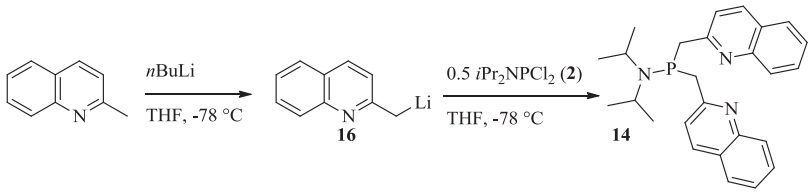
2.2.1. NMR properties. Tables 1–3 contain the ^1H, ^{13}C and ^{31}P NMR data of the new compounds **1**, **5**, **11**, **13** and **14** presented here. The phosphorus NMR chemical shift of **1** is with δ_P=144.4 in the same range as the corresponding signals of indolyl (143.8 ppm) and pyrrolyl (148.4 ppm) dichlorophosphine.[11] Worth mentioning are the small values of most P,C-couplings in the carbazolyl substituent. They have values between 1.3 and <0.5 Hz and only $^3J_{PC}$ is larger (Table 1). This applies to all carbazolyl substituted phosphines reported. The ^{31}P NMR shifts of the bis(picolyl) and bis(quinaldinyl)



Scheme 4. Synthesis of diisopropylamino bis(picolyl) phosphine (**11**) by direct reaction of 2 equiv of picolyl-lithium (**12**) with diisopropylamino dichlorophosphine (**2**).

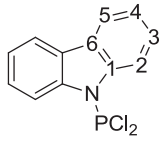


Scheme 5. Synthesis of carbazolyl bis(quinaldinyl) phosphine (**13**) by reaction of dichlorophosphine **1** with QuinTMS (**15**).



Scheme 6. Synthesis of diisopropylamino bis(quinaldinyl) phosphine (**14**) by reaction of dichlorophosphine **2** with quinaldinyl-lithium (**16**).

Table 1
^{1}H, ^{13}C and ^{31}P NMR data of carbazolyl dichlorophosphine **1**. Chemical shifts δ in ppm, coupling constants J in Hz



1

δ_C		δ_P	144.4
C1	139.6		
$^{2}J_{PC}$	<0.5	δ_H	
C2	114.4	H2	8.02–7.99
$^{3}J_{PC}$	15.7		
C3	126.7	H3	7.52–7.48
$^{4}J_{PC}$	1.3		
C4	123.2	H4	7.41–7.37
$^{5}J_{PC}$	1.3		
C5	120.7	H5	8.05–8.00
$^{4}J_{PC}$	<0.5		
C6	123.5		
$^{3}J_{PC}$	<0.5		

phosphines are all four in the same region between 34.8 (**13**) and 42.4 (**11**) ppm and are typical for amino phosphines.[12] The chemical shift of the phosphorus atoms of the carbazolyl substituted phosphines are in both cases shifted to higher field, as compared to the corresponding NMR signals of the *iso*propyl substituted derivatives.

In compounds **5**, **11**, **13** and **14** the CH_2 protons are diastereotopic. For all compounds except **13** the diastereotopy is clearly visible in the ^{1}H NMR spectra, where the typical AB part of an ABX spectrum (X=P) is observed. The signal of the CH_2 protons of compound **13** is just a broad singlet (The signals of the respective CH_2 protons are depicted next to Tables 2 and 3).

*2.2.2. Molecular and crystal structures of dichlorophosphines **1** and **3**.* Single crystals suitable for X-ray diffraction of the dichlorophosphines **1** and **3** were obtained by storing a solution of the compound at −18 °C (Et_2O (**1**), pentane (**3**)). Both compounds crystallize in an orthorhombic space group with four ($P2_12_12_1$ (**1**)) and eight (*Pbca* (**3**)) formula units per unit cell, respectively. In both cases the asymmetric units consist of one molecule of the compound (Fig. 1).

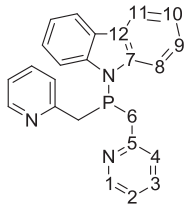
In the molecular structures of **1** and **3**, all P–Cl bond lengths are different (2.086(8) Å/2.056(8) Å (**1**) and 2.046(1) Å/2.105(1) Å (**3**)) (Table 4). This is in contrast to the similar lengths of the P–Cl bonds in the crystal structures of the literature known Me_2NPCl_2 (2.095(1) Å)[13] and Cy_2NPCl_2 (2.092(8) Å).[14] Reason for the largest deviation, which occurs in the molecular structure of **3**, is most probably negative hyperconjugation[15] of the lone pair of the nitrogen atom to the anti bonding σ*-orbital of the P1–Cl2 bond. Similar interaction in dichlorophosphines $RPCl_2$ with suitable substituents R have been reported in the literature.[16]

All four P–Cl bonds are longer than the literature values for a P–Cl single bond (2.04 Å,[17] 2.008 Å[18]) and the longest one is longer than the corresponding bond in the structure of Me_2NPCl_2. It is located under the longer bonds compared to those in other amino dichlorophosphines with the R_2NPCl_2 structural motive (see Fig. 2). The shorter P–Cl bonds in the crystal structures of **1** and **3** are the shortest P–Cl bonds in the family of amino dichlorophosphines R_2NPCl_2 (Fig. 2). They are in the range of P–Cl bonds observed in the molecular structures of amino bis(dichloro)phosphines $RN(PCl_2)_2$ (Fig. 2).

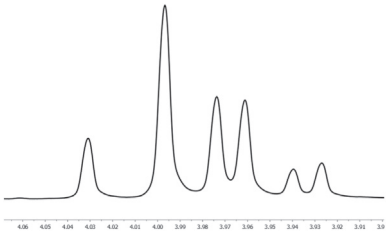
The two P–N bonds in the molecular structures of **1** (1.681(2) Å) and **3** (1.668(1) Å) are longer than the P–N bonds in Me_2NPCl_2[13] and Cy_2NPCl_2.[14] They are shorter than the literature value for a P–N single bond (1.76 Å).[17] The bond angles around the phosphorus atoms are in both structures very similar and in the expected range.

In the molecular structure of **1**, the phosphorus atom is not located in the plane of the planar carbazolyl substituent. The P1–N1–C1–C2 and the P1–N1–C12–C11 torsion angles are 7.5(3)° and −5.9(3)°, respectively. The Cl1–P1–Cl2 unit is twisted out of

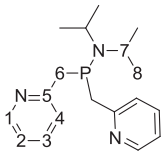
Table 2
^{1}H, ^{13}C and ^{31}P NMR data of the amino bis(picolyl)phosphines **5** and **11**. Chemical shifts δ in ppm, coupling constants J in Hz



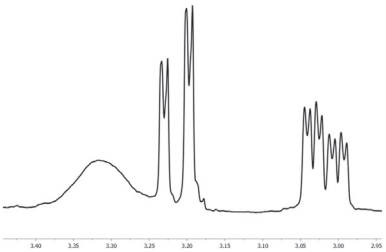
5



Signal of the CH_2 protons in the ^{1}H NMR spectrum of **5.**



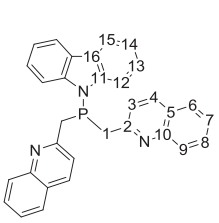
11



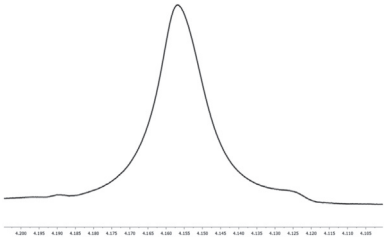
Signal of the CH_2 protons in the ^{1}H NMR spectrum of **11**. The broad signal belongs to *i*Pr-CH (H7).

	5	**11**		**5**	**11**
δ_P	37.6	42.2	δ_H		
$^{2}J_{PH}$	4.4	5.4	H1	8.42–8.40	8.41
δ_C			$^{3}J_{H1H2}$	4.6	4.4
C1	149.5	149.1	$^{4}J_{H1H3}$	—	1.9
$^{4}J_{PC}$	1.3	1.0	$^{5}J_{H1H4}$	—	0.9
C2	121.3	120.5	H2	6.93	6.96
$^{5}J_{PC}$	2.5	2.2	$^{3}J_{H2H3}$	7.3	7.7
CC3	136.5	135.9	$^{4}J_{H2H4}$	1.0	1.1
$^{4}J_{PC}$	1.3	1.0	H3	7.33–7.28	7.46
C4	123.6	123.9	$^{3}J_{H3H4}$	7.8	6.8
$^{3}J_{PC}$	5.5	6.6	H4	6.83	7.20
C5	157.0	159.2	ν_{H6A}	3.95	3.02
$^{2}J_{PC}$	9.5	8.9	ν_{H6B}	4.01	3.21
C6	37.1	40.2	$^{2}J_{PH6A}$	5.1	6.2
$^{1}J_{PC}$	20.4	21.0	$^{2}J_{PH6B}$	<0.5	<0.5
C7	139.7	45.5	$^{2}J_{H6AH6B}$	13.7	13.2
$^{2}J_{PC}$	<0.5	<0.7	H7	—	3.31
C8	113.3	23.7	$^{3}J_{H7H8}$		6.8
$^{3}J_{PC}$	12.2	5.9	H8	7.86	0.82
C9	125.9		$^{3}J_{H8H9}$	8.5	—
$^{4}J_{PC}$	1.1		$^{4}J_{PHS}$	—	3.1
C10	120.5		H9	7.37	—
$^{2}J_{PC}$	<0.5		$^{3}J_{H9H10}$	7.6	—
C11	120.2		H10	7.22	—
$^{4}J_{PC}$	<0.5		$^{3}J_{H10H11}$	7.5	—
C12	124.8		H11	8.00	—
$^{3}J_{PC}$	5.2				

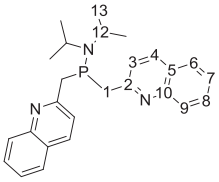
Table 3
^{1}H, ^{13}C and ^{31}P NMR data of the amino bis(quinaldinyl) phosphines **13** and **14**. Chemical shifts δ in ppm, coupling constants J in Hz



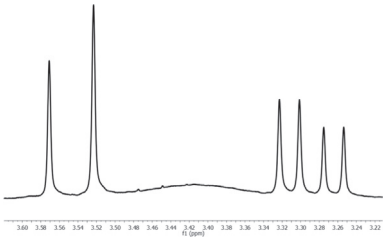
13



Signal of the CH_2 protons in the ^{1}H NMR spectrum of **13**.



14



Signal of the CH_2 protons in the ^{1}H NMR spectrum of **14**. The broad signal belongs to *i*Pr-CH (H12).

	13	**14**		**13**	**14**
δ_P	34.8	39.8	δ_H		
$^{2}J_{PH}$, $^{3}J_{PH}$	<2.0	5.5	H1	4.26	
δ_C			ν_{H1A}		3.30
C1	38.2	41.5	ν_{H1B}		3.55
$^{1}J_{PC}$	21.4	21.8	$^{2}J_{H1AH1B}$		13.0
C2	157.65	159.6	$^{2}J_{PHA}$		5.9
$^{2}J_{PC}$	10.5	9.2	$^{2}J_{PHB}$		<0.1
C3	121.8	122.4	H3	7.05	7.40
$^{3}J_{PC}$	5.0	6.6	$^{3}J_{H3H4}$	8.4	8.6
C4	136.5	135.7	H4	7.80	7.96
C5	126.7	126.5	$^{3}J_{H4H15}$	7.7	—
$^{5}J_{PC}$	1.7	1.4	H6	7.62	7.69
C6	127.5	127.5	$^{3}J_{H6H7}$	7.7	8.1
$^{6}J_{PC}$	0.9	0.7	$^{4}J_{H6H8}$		1.3
C7	126.0	125.5	H7	7.43–7.38	7.44–7.40
$^{7}J_{PC}$	<0.4	0.7	$^{3}J_{H7H8}$		7.3
C8	129.5	129.2	H8	7.60–7.57	7.61
C9	128.9	128.8	$^{3}J_{H8H9}$	8.6	8.5
$^{5}J_{PC}$	<0.4	0.4	H9	7.86	7.99
C10	148.0	148.0	H12	7.99	3.42
$^{4}J_{PC}$	<0.4	0.9	$^{3}J_{H12H13}$	7.5	6.7
C11	144.0	—	$^{3}J_{PH12}$	2.1	—
C12	113.6	45.7	H13	7.30–7.24	0.88
$^{3}J_{PC}$	12.4	<0.5	H14	7.43–7.38	—
C13	120.6	23.7	H15	8.04	—
$^{4}J_{PC}$	<0.4	5.3			
C14	110.8	—			
C15	120.3	—			
C16	125.9	—			
$^{3}J_{PC}$	0.5				

the aromatic plane in a way that the chlorine atoms are almost symmetrically located under and over the plane (Fig. 3). A similar arrangement can be found in the molecular structure of Cy_2NPCl_2.[14] In contrast to the symmetric alignment of the chlorine atoms discussed before, the substituents at phosphorus and nitrogen in **3** are twisted relative to each other in the solid state (Fig. 1 middle and right). The P1–Cl2 bond and the N1–C7 bond are almost perpendicular to each other and the respective torsion angle Cl2–P1–N1–C7 is −92.2° (see Fig. 1).

In the crystal the molecules of compound **1** are arranged along the *a*-axis by intermolecular π-stacking interactions (Fig. 3). The molecules in the crystal structure of **3** are connected along the *b*-axis by non-classical C–H···π hydrogen bonds (Fig. 4).

*2.2.3. Molecular and crystal structures of the phosphines **5** and **14**.* Single crystals suitable for X-ray diffraction of carbazolyl bis(-picolyl) phosphine (**5**) and diisopropylamino bis(quinaldinyl) phosphine (**14**) were obtained by storing a solution of the compound in toluene at 0 °C (**5**) or −18 °C (**14**), respectively. Compound **5** crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell whereas **14** crystallizes in the orthorhombic space group *Pbca* with eight formula units in the unit cell. In both cases the asymmetric unit comprises one molecule of the compound (Fig. 5). Table 5 contains selected bond lengths and angles from both molecular structures.

The P1–N1 bond in **5** (1.744(1) Å) is longer than the P1–N1 bond in **14** (1.672(3) Å) and also longer than the P–N bonds in the

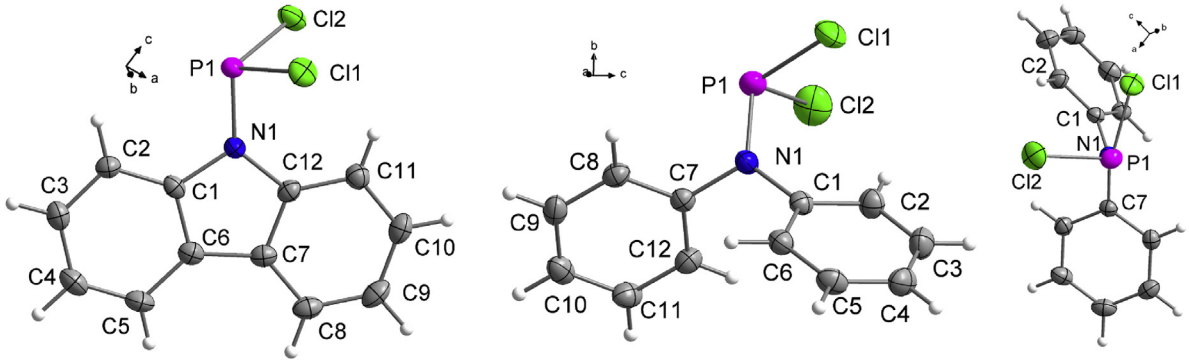


Fig. 1. Asymmetric units of the dichlorophosphines **1** (left) and **3** (middle and right). Thermal ellipsoids are drawn at 50% probability level.

Table 4
Selected bond lengths [Å] and angles [°] in the molecular structures of the aminodichloro phosphines **1** and **3**

	1	**3**
P1–N1	1.681(2)	1.668(1)
P1–Cl1	2.086(8)	2.046(1)
P1–Cl2	2.056(8)	2.105(1)
N1–P1–Cl1	101.0(7)	101.1(1)
N1–P1–Cl2	102.1(6)	104.5(2)
Cl1–P1–Cl2	97.7(3)	98.8(1)

molecular structures of the dichlorophosphines discussed above, whereas the bond in **14** is in the same range as the corresponding bonds in **1** and **3**. Both P–N bonds are shorter than the literature value for a P–N single bond (1.76 Å).[17] The two P–C bond lengths in the respective structures are similar and those in **14** are longer than the P–C bonds in **5** (Table 5). All four P–C bonds are in the range of a P–C single bond (1.855 Å)[18] and comparable to the corresponding bonds in the molecular structure of Pic_3P.[3b]

The phosphorus atom in the molecular structure of **5** is surrounded pyramidal by two carbon atoms and one nitrogen atom. The sum of the angles at phosphorus is 303.6°. The nitrogen atom of the carbazolyl substituent is not in a planar surrounding (Fig. 5 middle),

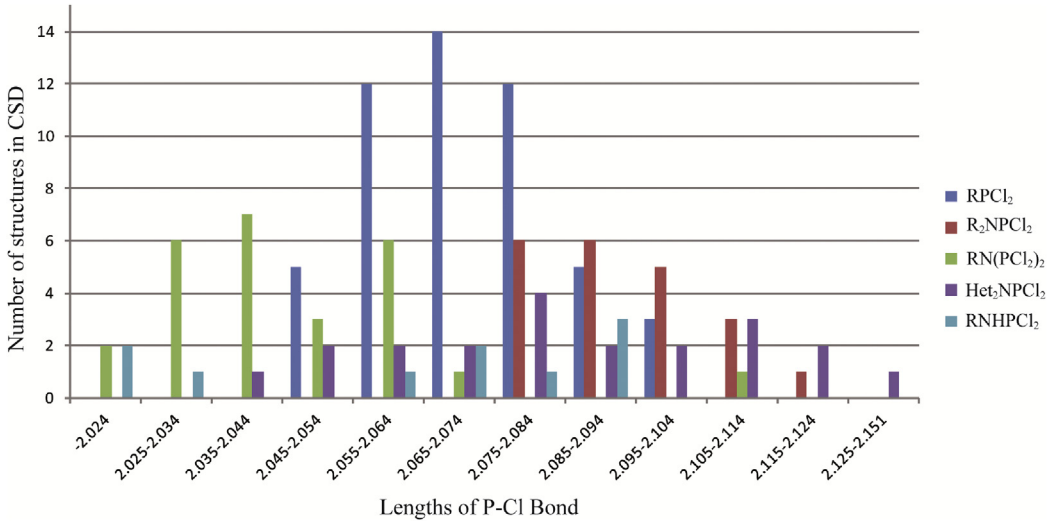


Fig. 2. Statistical distribution of P–Cl bond lengths from crystal structures of the CSD (Cambridge Structural Database), 47 in total. R=Aryl, Alkyl; Het=Heteroatom, e.g. P, N, Si.

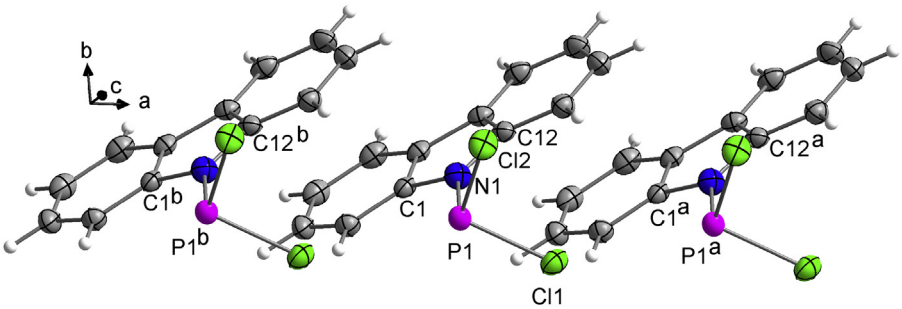


Fig. 3. π-stacking in the crystal structure of carbazolyl dichlorophosphine (**1**), $d(C_g(2)\cdots C_g(3)^b)$=3.738(1) Å; C_g=Center of gravity of the aromatic ring; $C_g(2)$ is the ring C1–C6; $C_g(3)$ is the ring C7–C12. Symmetry codes: a (1+x, y, z), b (−1+x, y, z). Thermal ellipsoids are drawn at 50% probability level.

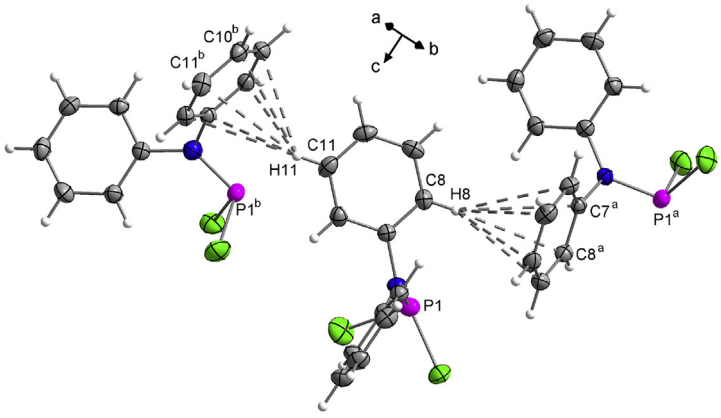


Fig. 4. Non-classical C–H···π hydrogen bonds in the crystal structure of diphenylamino dichlorophosphine (**3**). d(C8···C_g(2)^a)=3.723(2) Å, d(C11···C_g(2)^b)=3.697(2) Å. C_g(2) is the center of gravity of the ring C7–C12. Symmetry codes: a (1−x, 0.5+y, 1.5−z), b (1.5−x, −0.5+y, z). Thermal ellipsoids are drawn at 50% probability level.

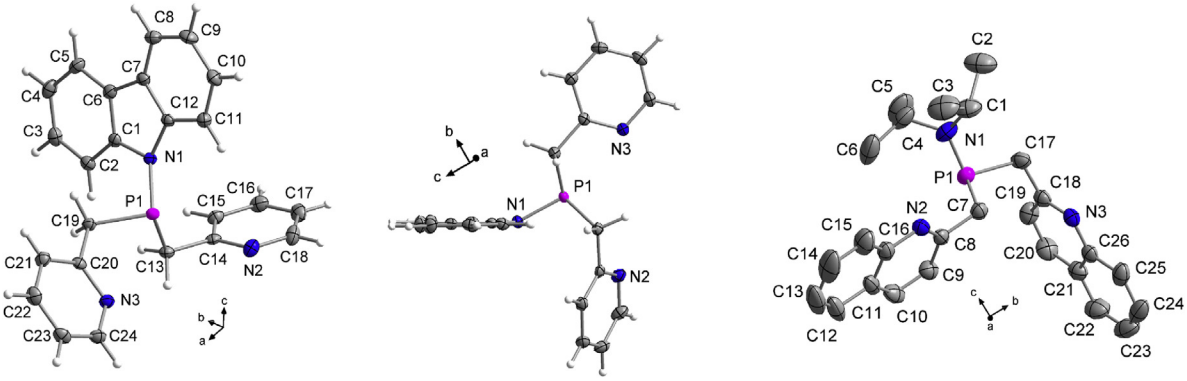


Fig. 5. Left and middle: Asymmetric unit of **5**. Right: Asymmetric unit of **14**, H atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

Table 5
Selected bond lengths [Å] and angles [°] in the molecular structures of **5** and **14**

	5		**14**
P1–N1	1.744(1)	P1–N1	1.672(3)
P1–C13	1.849(2)	P1–C7	1.862(3)
P1–C19	1.856(2)	P1–C17	1.867(8)
N1–P1–C13	101.8(6)	N1–P1–C7	104.4(1)
N1–P1–C19	99.4(6)	N1–P1–C17	103.8(1)
C13–P1–C19	102.4(7)	C7–P1–C17	98.5(1)
P1–N1–C1–C2	−35.7(2)		
P1–N1–C12–C11	31.2(2)		

and as a consequence the phosphorus atom is not in the same plane as the carbazolyl substituent as it can be observed in the structure of **1**. The corresponding torsion angles are with 31.2(2)° and −35.7(2)° (Table 5) clearly larger than the respective torsion angles in **1**.

In the crystal, the molecules of **5** are interconnected by C–H···π hydrogen bonds to form a complex network (Fig. 6). In the crystal structure of **14**, the molecules are interconnected by C25–H25···N2 hydrogen bonds to form dimers. These dimers form chains parallel to the *b*-axis by π-stacking interactions between the quinaldinyl substituents containing the hydrogen bond acceptor N2 (Fig. 7).

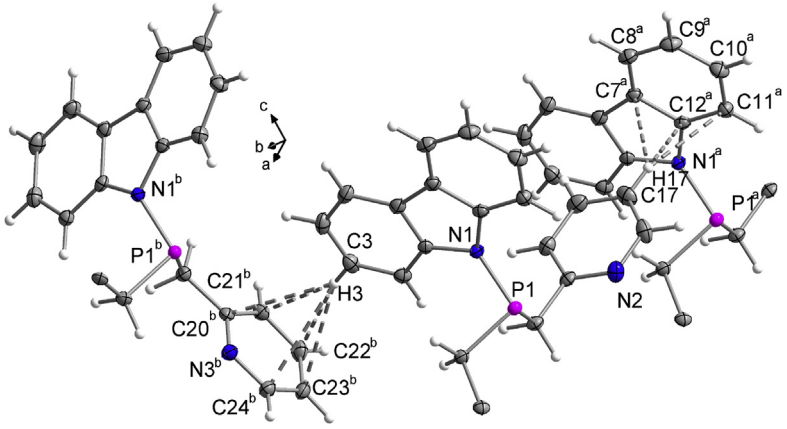


Fig. 6. Non classical C–H···π hydrogen bonds in the crystal structure of **5**. The picolyl substituents, which do not participate in intermolecular hydrogen bonding are omitted for clarity. d(C3···C_g(3)^b)=3.894(2) Å, d(C17···C_g(5)^a)=3.569(2) Å, C_g is the center of gravity of the aromatic ring, C_g(3) contains N3, C_g(5) is the ring C7–C12. Symmetry code: a (x, −1+y, z), b (0.5+x, 0.5−y, 0.5+z). Thermal ellipsoids are drawn at 50% probability level.

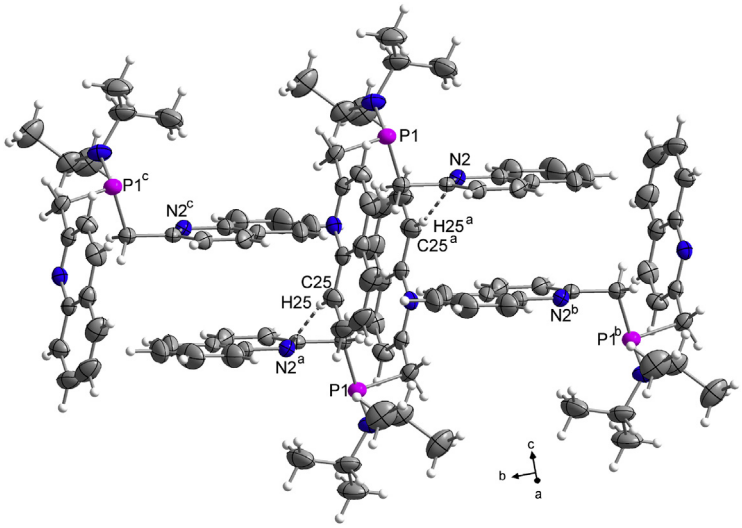


Fig. 7. C25–H25···N2 hydrogen bonds and π-stacking interactions in the crystal structure of **14**. d(C25···N2^a)=3.501(1) Å, d(C$_g$(1)···C$_g$(1)^b)=3.723(1) Å. C$_g$(1) contains N2. Symmetry codes: a (1−x, 1−y, −z), b (1−x, −y, −z), c (x, 1+y, z). Thermal ellipsoids are drawn at 50% probability level.

3. Conclusion

Two new amino bis(picolyl) (**5** and **11**) and amino bis(quinaldinyl) (**13** and **14**) substituted phosphines were synthesized and isolated in acceptable to very good yields. The synthetic route via the reaction of the respective dichlorophosphines **1** and **2** and the trimethyl(silyl) derivatives of picoline or quinaldine is only applicable for the carbazolyl substituted dichlorophosphine **1**. Dichlorophosphine **2** does not react with either **6** or **15**. In this case the lithiated derivatives of picoline and quinaldine **12** and **16** were used.

The study shows once more the special properties of the benzylic position in 2-picoline. In fact the P–C bond in $PicPCl_2$ (**9**) proves to be quite labile, as demonstrated by the easy dismutation of $PicPCl_2$ (**9**) observed.

The straightforward and easy access of the new amino bis(picolyl) and amino bis(quinaldinyl) phosphines opens the way for a systematic study of their complex chemistry in particular regarding their applicability as ligands in luminescent and catalytically active transition metal complexes.

4. Experimental procedures

4.1. General information

All chemicals were commercially available and were used as received. NMR spectra were recorded with a JEOL EX 400 Eclipse instrument operating at 400.128 MHz (^{1}H) and 100.626 MHz (^{13}C). Chemical shifts are referred to Me_4Si (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. All spectra were measured, if not mentioned otherwise, at 25 °C. The assignment of the signals in the ^{1}H and ^{13}C NMR spectra is based on 2D (^{1}H,^{1}H–COSY45, ^{1}H, ^{13}C–HMQC and ^{1}H, ^{13}C-HMBC) experiments. For the HMBC NMR spectra a sinebell window function and a zero filling in both directions was applied resulting in a 4k×4k matrix. Mass spectrometric data were obtained with a JEOL Mstation JMS 700 spectrometer using the direct EI mode. Elemental analysis was performed either on an Elementar Vario El analysator or an Elementar vario micro cube for C, H and N. The molecular structures in the crystalline state were determined by single crystal X-ray diffraction. For data collection an Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD detector with an X-ray radiation wavelength of 0.71073 Å was used. The data collection was performed with the CrysAlis CCD software[19] and the data reduction with the CrysAlis RED software.[20] The structures were solved with SIR-92, refined with SHELXL-97 and finally checked using PLATON.[21] The absorptions were corrected by SCALE3 ABSPACK multiscan method.[22] All relevant data and parameters of the X-ray measurements and refinements are given in Table 6. Additional structural data like bond lengths and angles can be found in the Supplementary data. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1453459 (**1**), CCDC 1453462 (**3**), CCDC 1453460 (**5**) and CCDC 1453461 (**14**) (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

4.2. Synthetic procedures

*4.2.1. Carbazolyl dichlorophosphine (**1**).* Carbazole (8.0 g, 47.8 mmol) was dissolved in 180 mL of dry THF and cooled to 0 °C. TEA (1.5 equiv, 10 mL, 71.7 mmol) and PCl_3 (1.4 equiv, 6 mL, 68.8 mmol) were added dropwise while stirring. The reaction mixture was allowed to reach ambient temperature over night. The colorless precipitate was removed by filtration and the solvent removed in vacuo. The crude product was extracted with 50 mL of dry Et_2O. The colorless precipitate was removed by filtration and the solvent removed in vacuo. 9-(Dichloro)-9*H*-carbazole (**1**) was obtained as colorless to yellow air and moisture sensitive voluminous solid (54%, 6.9 g, 25.8 mmol).

EA: calcd for $C_{12}H_8Cl_2NP$: C: 53.76%, H: 3.01%, N: 5.22%, found: C: 54.92 (+1.16) %, H: 3.66 (+0.65) %, N: 5.03 (−0.19) %.

NMR: see Table 1.

*4.2.2. 2-((Trimethylsilyl)methyl)quinoline (**15**).*[10] Quinaldine (3.39 mL, 25 mmol) was dissolved in 50 mL of dry THF and cooled to −78 °C. *n*BuLi (1 equiv, 15.6 mL, 1.6 M in hexane) was added dropwise while stirring. The reaction mixture was stirred for additional 30 min and TMSCl (1.2 equiv, 3.5 mL, 30 mmol) was added dropwise. The reaction mixture was allowed to reach room temperature over night. The solvent was removed in vacuo and the

Table 6
Structural data of the compounds **1**, **3**, **5** and **14**

	1	**3**	**5**	**14**
Sum formula	$C_{12}H_8Cl_2NP$	$C_{12}H_{10}Cl_2NP$	$C_{24}H_{20}N_3P$	$C_{26}H_{30}N_3P$
Molar mass [g·mol^{-1}]	268.06	270.08	381.40	415.50
Crystal size [mm^3]	0.20×0.15×0.05	0.26×0.22×0.16	0.32×0.28×0.26	0.40×0.20×0.20
T [K]	173(2)	173(2)	173(2)	173(2)
Color, habitus	Colorless plate	Colorless block	Colorless block	Colorless block
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$Pbca$ (No. 61)	$P2_1/n$ (No. 14)	$Pbca$ (No. 61)
a [Å]	5.5020(2)	13.5711(7)	14.1930(3)	21.5450(6)
b [Å]	11.5270(4)	7.0664(3)	8.6950(8)	8.8310(2)
c [Å]	18.0370(6)	25.2844(11)	16.8150(8)	25.2600(6)
α [°]	90	90	90	90
β [°]	90	90	113.052(6)	90
γ [°]	90	90	90	90
V [Å^3]	1143.93(7)	2424.74(2)	1909.4(2)	4806.1(2)
Z	4	8	4	8
Wavelength [Å]	MoKα 0.71069	MoKα 0.71069	MoKα 0.71069	MoKα 0.71069
ρ_{calcd} [g cm^{-3}]	1.556	1.480	1.327	1.148
μ(MoK_α) [cm^{-1}]	0.674	0.637	0.159	0.131
F(000)	544	1104	800	1776
hkl range	$-7\le h\le 7$	$-18\le h\le 16$	$-18\le h\le 18$	$-24\le h\le 26$
	$-14\le k\le 15$	$-8\le k\le 9$	$-9\le k\le 11$	$-11\le k\le 11$
	$-23\le l\le 24$	$-33\le l\le 33$	$-16\le l\le 22$	$-31\le l\le 31$
Refl.collected	10599	2072	17,490	7851
Refl. independent	2827	2996	4725	4883
Refl. observed	2538	2150	3917	3796
R_{int}	0.0407	0.0641	0.0297	0.0463
Parameter	153	155	271	291
θ-range [°]	$4.20\le\theta\le 28.27$	$4.16\le\theta\le 28.28$	$4.25\le\theta\le 28.28$	$4.29\le\theta\le 28.99$
R_1, wR_2 [I>2σ(I)]	0.0324, 0.0719	0.0396, 0.0815	0.0387, 0.0917	0.0420, 0.0992
R_1, wR_2 (all data)	0.0395, 0.0758	0.0668, 0.0946	0.0503, 0.0988	0.0582, 0.1084
GooF	1.064	1.060	1.035	1.026
δp_{max}, δp_{min} [e·Å^{-3}]	0.253, −0.210	0.359, −0.338	0.376, −0.277	0.220, −0.266

crude product was extracted with 25 mL of dry pentane. The colorless precipitate was removed by filtration and the solvent removed in vacuo. The crude product was purified by vacuum distillation (65 °C, $2.6\cdot10^{-2}$ mbar, 80 °C oilbath) and obtained as a colorless liquid (77%, 4.16 g, 17.3 mmol).

^{29}Si{^{1}H} NMR (79.43 MHz, $CDCl_3$): δ=3.4. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ=162.0 (C_{Ar}), 148.2, (C_{Ar}), 135.7 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (C_{Ar}), 127.5 (C_{Ar}), 125.9 (C_{Ar}), 125.0 (C_{Ar}), 121.8 (C_{Ar}), 31.6 (CH_2), −1.4 (CH_3).

H NMR (270.17 MHz, $CDCl_3$): δ=8.00–7.91 (m, 2H, H_{Ar}), 7.72–7.68 (m, 1H, H_{Ar}), 7.65–7.59 (m, 1H, H_{Ar}), 7.43–7.36 (m, 1H, H_{Ar}), 7.07 (d, 1H, J=8.4 Hz, H_{Ar}), 2.54 (s, 2H, CH_2), −0.04 (s, 9H, $SiCH_3$).

*4.2.3. Carbazolyl bis(picolyl)phosphan (**5**).* Carbazolyl dichlorophosphine (**1**) (5.36 g, 20 mmol) was dissolved in 30 mL of dry THF and cooled to 0 °C. PicTMS (**6**) (2 equiv, 6.61 g, 40 mmol) was added dropwise while stirring. The reaction mixture was allowed to reach room temperature over night and the solvent was removed in vacuo. The crude product was extracted with 25 mL of dry Et_2O and the precipitate was removed by filtration and the solvent removed in vacuo. Phosphine **5** was obtained as a colorless to yellowish solid that is highly sensitive towards oxidation (92%, 7.02 g, 18.4 mmol).

EA: calcd for $C_{24}H_{20}N_3P$: C: 75.58%, H: 5.29%, N: 11.02%, found: C: 75.57 (−0.01) %, H: 5.35 (+0.06) %, N: 10.88 (−0.14) %.

HRMS (DEI): Mass calcd for $C_{24}H_{20}N_3P$: 381.1395, measured: 381.1399 (M^+, 100%).

NMR: see Table 2.

*4.2.4. N,N-diisopropylamino bis(picolyl) phosphine (**11**).* Picoline (2 equiv, 0.99 mL, 10 mmol) was dissolved in 10 mL of dry THF and cooled to −78 °C. *n*BuLi (2 equiv, 6.25 mL, 1.6 M in hexane) was added dropwise while stirring. The dark red reaction mixture was stirred for another hour. In a second schlenk flask, iPr$_2$NPCl$_2$ (1 equiv, 1.01 g, 5 mmol) was dissolved in 5 mL of dry THF at −78 °C. To this solution the dark read solution of Picolyl-Lithium (**12**) was added dropwise via a cannula. The reaction mixture was allowed to reach room temperature over night and the solvent was removed in vacuo. The crude product was extracted with 20 mL of dry pentane and the colorless precipitate was removed by filtration. The solvent was removed in vacuo to yield **10** as a yellowish air and moisture sensitive solid (32%, 1.01 g, 3.2 mmol).

NMR: see Table 2.

*4.2.5. Carbazolyl bis(quinaldinyl) phosphine (**13**).* Carbazolyl dichlorophosphine (**1**) (1 equiv, 2.19 g, 8.17 mmol) was dissolved in 40 mL of dry THF and cooled to 0 °C. QuinTMS (**15**) (2 equiv, 3.52 g, 16.34 mmol) was added dropwise while stirring. The reaction mixture was allowed to reach room temperature over night and the solvent was removed in vacuo. The crude product was washed three times with 20 mL of dry Et_2O to yield **13** as a yellow to orange air and moisture sensitive solid (89%, 3.49 g, 7.25 mmol).

EA: calcd for $C_{32}H_{24}N_3P$: C: 79.82%, H: 5.02%, N: 8.73%, found: C: 77.76 (−2.06) %, H: 5.26 (+0.24) %, N: 8.27 (−0.46) %.

HRMS (DEI): Mass calcd for $C_{32}H_{24}N_3P$: 481.1708, measured: 481.1689 (M^+, 78.5%).

NMR: see Table 3.

*4.2.6. N,N-diisopropylamino bis(quinaldinyl) phosphine (**14**).* Quinaldine (2 equiv, 2.71 g, 20 mmol) was dissolved in 25 mL of dry THF and cooled to −78 °C. *n*BuLi (2 equiv, 12.5 mL, 1.6 M in hexane) was added dropwise while stirring. The dark red reaction mixture was stirred for another hour. In a second schlenk flask, iPr$_2$NPCl$_2$ (1 equiv, 2.02 g, 10 mmol) was dissolved in 10 mL of dry THF at −78 °C. To this solution the dark read solution of quinaldinyllithium (**16**) was added dropwise via a cannula. The reaction mixture was allowed to reach room temperature over night and the solvent was removed in vacuo. The crude product was extracted with 50 mL of dry toluene and the colorless precipitate was removed by

filtration. The solvent was removed in vacuo to yield **13** as a yellowish air and moisture sensitive solid (94%, 3.91 g, 9.42 mmol).

EA: calcd for $C_{26}H_{30}N_3P$: C: 75.16%, H: 7.28%, N: 10.11%, found: C: 74.36 (−0.80) %, H: 7.34 (+0.06) %, N: 9.89 (−0.22) %.

HRMS (DEI): Mass calcd for $C_{26}H_{30}N_3P$: 415.2177, measured: 415.2199 (M^+, 100%).

NMR: see Table 3.

*4.2.7. Picolyldichlorophosphine (9)/Bis(picolyl)chlorophosphine (**10**).* PicTMS (**6**) (1 mmol, 165.1 mg) was dissolved in a 1:1 mixture of dry THF and Et_2O (5 mL) and added dropwise to a solution of PCl_3 (1 equiv, 0.087 mL, 1 mmol) at −78 °C. The reaction mixture was allowed to reach ambient temperature over night and the solvent was removed in vacuo. The ^{31}P NMR spectrum after this step reveals a 1.3:1 mixture of **10** and **9**, respectively.

NMR: **9**: ^{31}P NMR (161.99 MHz, THF): δ=183.3 (t, $^2J_{PH}$=12.2 Hz), 40%. **10**: ^{31}P NMR (161.99 MHz, $CDCl_3$): δ=96.4, (quint, $^2J_{PH}$=8.9 Hz), 53%.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.04.021.

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