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# Synthesis of Hemilabile P,N Ligands: $\omega$-2-Pyridyl-*n*-alkylphosphines

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**Summary.** A series of P,N ligands of the general formula (2-*py*)-$(CH_2)_n$-P$R_2$ (2-*py*: 2-pyridyl; *R*: *i*-Pr ($n = 1$, 4–7), Ph ($n = 5$–7)) **4a–g** and **6a** has been synthesized. Starting from 2-picoline (**1**), 2-($\omega$-chloroalkyl)pyridines **3a–d** are prepared. The reactions of **3a–d** with $(i\text{-Pr})_2$PLi and $Ph_2$PLi, respectively, result in the title compounds **4a–g** in up to 89% yield. Reaction of Cl-$(CH_2)_3$-P$(i\text{-Pr})_2$ with 2-picolyllithium (**2**) is an alternative route to **4a**. Additionally, P,P,N ligands **7a** and **9** are synthesized by similar methods. All new compounds were fully characterized. The formation of cyclic pyridinium derivatives **5a** and **5b** from intramolecular $S_N$ reactions of **3a** and **3b** is discussed in detail.

**Keywords.** Hemilabile ligand; P,N Ligand.

**Synthese hemilabiler P,N-Liganden: $\omega$-2-Pyridyl-*n*-alkylphosphine**

**Zusammenfassung.** Ausgehend von 2-Picolin (**1**) werden die homologen P,N-Liganden (2-*py*)-$(CH_2)_n$-P$R_2$ (2-*py*: 2-Pyridyl; *R*: *i*-Pr ($n = 1$, 4–7), Ph ($n = 5$–7) **4a–g** und **6a** dargestellt. Über die entsprechenden 2-($\omega$-Chloralkyl)pyridine **3a–d** erhält man durch nachfolgende Umsetzung mit $(i\text{-Pr})_2$PLi bzw. $Ph_2$PLi die Titelverbindungen **4a–g** in bis zu 89% Ausbeute. Alternativ erhält man Verbindung **4a** durch Umsetzung von Cl-$(CH_2)_3$-P$(i\text{-Pr})_2$ mit 2-Picolyllithium (**2**). Ähnliche Synthesemethoden eröffnen einen einfachen Zugang zu den P,P,N-Liganden **7a** und **9**. Alle neuen Verbindungen wurden vollständig charakterisiert. Die Bildung der zyklischen Pyridiniumderivate **5a** und **5b** durch intramolekulare $S_N$-Reaktionen von **3a** bzw. **3b** wird im Detail diskutiert.

## Introduction

Bidentate ligands which offer two different coordination sites are termed to be hemilabile [1]. They provide interesting properties in catalytic reactions: Fixed at the metal centre by one strong donor group, the number of coordination sites may be varied by addition or removal of the weaker donor group. This hemilability may play an important role during a catalytic cycle because key intermediates are often stabilized by weaker donor ligands, *e.g.* solvent molecules. Most recently, we were able to show that $\omega$-cyano-*n*-alkylphosphines exhibit an extraordinary effect on the cooligomerization of 1,3-butadiene and carbon dioxide due to labile bonding of the nitrile backbone to the active centre [2, 3]. Consequently, catalysts with hemilabile

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ligands may decrease the enthalpy of activation for fundamental reactions of the catalytic cycle.

Similar P,N ligands with one phosphino and one pyridyl moiety have attracted considerable interest in the remaining decade [4]. They offer unique properties in some catalytic reactions like the alkoxycarbonylation of alkynes [5]. Other recent fields of interest are the synthesis of heterobimetallic complexes [6] or studies on novel organic reactions [7]. Phosphinopyridines are often fixed in sterically rigid systems: As ligands, they tend to form stable *cis* chelate complexes [4]. Phosphinopyridines with $(CH_2)_n$ chains ($n > 3$) as spacers are rare [8]. Increasing the number of spacer atoms should decrease the tendency to form chelate complexes and therefore might have a significant influence on catalytic processes.

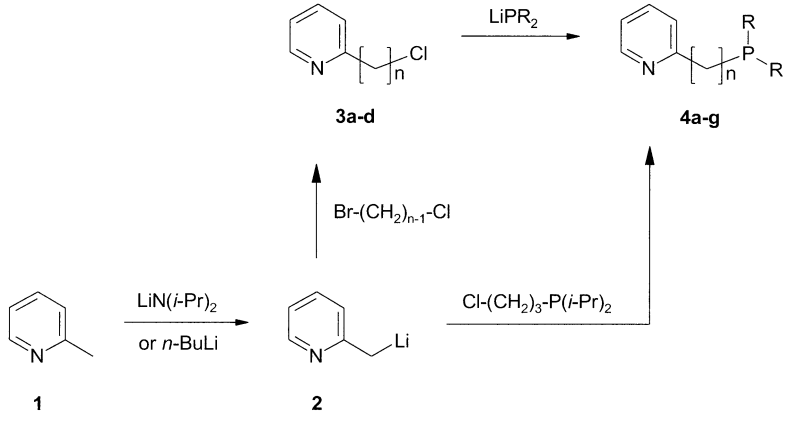
In order to study the behaviour of phosphinopyridines with variable spacer lengths in catalytic systems as well as in the formation of mononuclear complexes, our aim was to establish their synthetic approach. In this report, we describe the preparation and properties of a variety of $\omega$-2-pyridyl-*n*-alkylphosphines and of some related P,P,N ligands.

## Results and Discussion

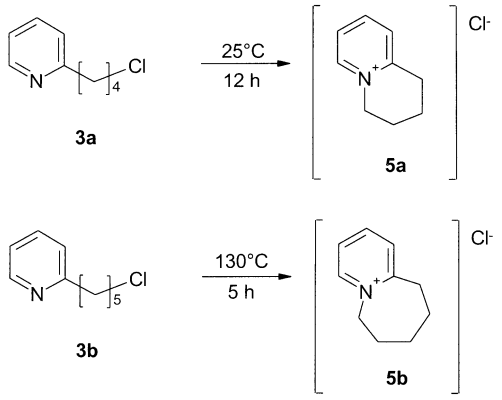
$\alpha$-Metalation of 2-picoline (**1**) provides an easy access to further substitution with alkyl halides [9]. Two routes for the syntheses of $\omega$-2-pyridyl-*n*-alkylphosphines were examined (Scheme 1).

After metalation of **1**, the reaction with $\alpha$-bromo-$\omega$-chloro-*n*-alkanes affords **3a–d** in up to 94% yield. Interestingly, **3a** and **3b** undergo intramolecular $S_N$ reactions to chlorides **5a** and **5b** (Scheme 2). Similar cyclic pyridinium salts have been synthesized by other methods [10–12]. The C,N stretching frequencies of the pyridine moiety shift from 1561 and 1591 $cm^{-1}$ to 1635 and 1583 $cm^{-1}$, indicating a positive charge at the nitrogen. In particular, all attempts to purify **3a** result in low yield.

**3c** and **3d** do not yield cyclic pyridinium salts as consecutive products. Obviously, the reaction is controlled by the formation of thermodynamically favoured ring sizes in the case of **3a** and **3b**. Molecular mass determination of **5a**




**Scheme 1.** Synthesis of **4a–d** (*R*: *i*-Pr, $n = 4$–7) and **4e–g** (*R*: Ph, $n = 5$–7)




**Scheme 2.** Intramolecular reactions of **3a** and **3b**

*via* measuring the osmotic pressure in chloroform solution indicates the existence of a dimer species. Dimers are also indicated by the FAB mass spectrum of **5a** and the EI mass spectrum of **5b**, whereas the EI mass spectrum of **5a** and the FAB mass spectrum of **5b** indicate monomeric structures. The NMR spectra of **5a** and **5b** are in good agreement with the analogous iodide derivatives reported by *Murphy et al.* [12, 13].

Attempts to quantify the reaction enthalpy of the ring closure reaction by differential scanning calorimetry were not successful because of interference of the exothermic reaction with rapid crystallization of nascent **5a** and **5b**, respectively. The reaction of **3a** in $CDCl_3$ solution is slow enough to be followed by NMR spectroscopy (Fig. 1). The rate constant of this first order reaction is calculated to be $1.38 \cdot 10^{-5}\,s^{-1}$ with a half time of 14 h at 298 K, corresponding to an

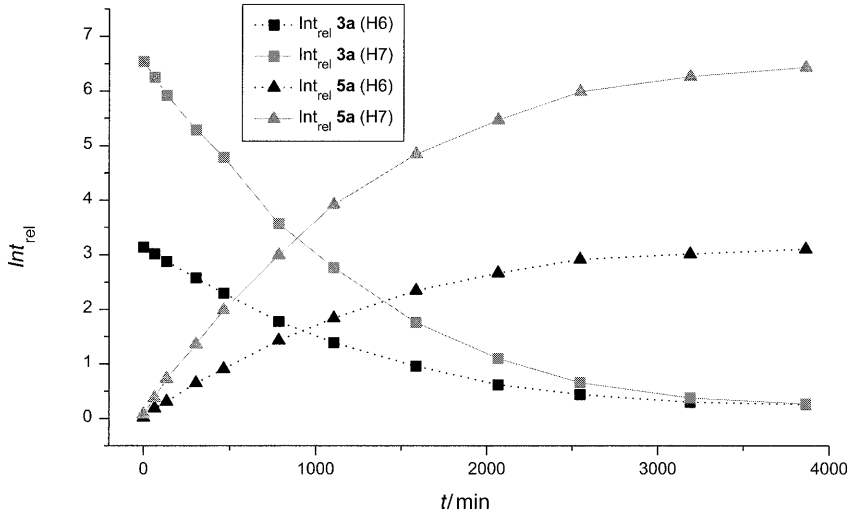



**Fig. 1.** Relative integral values of selected $^1$H NMR resonances for the reaction of **3a** to **5a** at 298 K (Scheme 2, Experimental); $\Sigma\ Int_{(H)}\ \{(Et_3Si)_2O\} = 100$

**Table 1.** Selected spectroscopic data of P,N and P,P,N ligands

| | $\delta(^{31}P)$/ppm | $\nu_{C=N}$/cm$^{-1}$ | Ref. |
|---|---|---|---|
| **4a** | 4.4 | 1590, 1569 | [a] |
| **4b** | 3.2 | 1590, 1569 | [a] |
| **4c** | 4.5 | 1590, 1569 | [a] |
| **4d** | 4.4 | 1590, 1569 | [a] |
| **4e** | −15.6 | 1589, 1566 | [a] |
| **4f** | −15.5 | 1598, 1586, 1567 | [a] |
| **4g** | −15.5 | 1587, 1568 | [a] |
| **6a** | 13.3 | 1591, 1567 | [a] |
| **6b** | −10.1[b] | 1589, 1580, 1567 [b] | [14] |
| **7a** | 12.6 | 1584, 1565 | [a] |
| **7b** | −4.5 | 1580 | [15] |
| **9** | 12.7 | 1587, 1573 | [a] |
| **10** | −9.1 | 1589, 1579, 1568 [b] | [17] |

[a] This work; [b]previously not reported, $^{31}P$ NMR spectra in $CDCl_3$

intramolecular pathway (Scheme 2). In *THF* solution, the ring closure of **3a** is very slow, and **3b** is fairly stable in most common solvents.

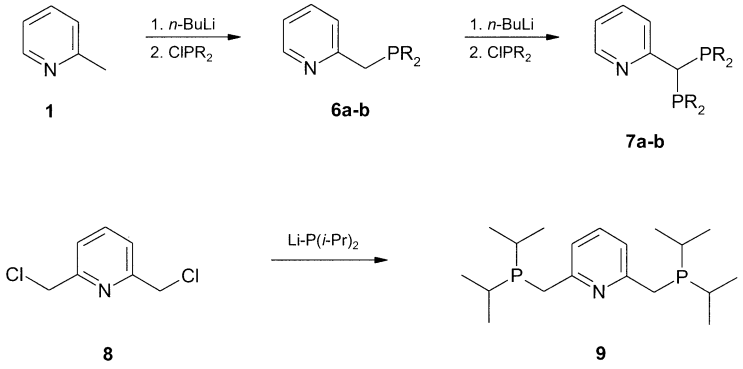
**3a** is less suitable than **3b–d** for further reaction with lithium phosphides (cf. Scheme 1). The desired products **4b–g** are obtained in 67–89% yield after purification. The yield of **4a** (9%) is low over both steps due to the low yield of **3a**. The analogous reaction of **3a** with $Ph_2PLi$ yields a product mixture: Attempts to purify the desired product by distillation or column chromatography have not been successful. **4a** may be alternatively synthesized (Scheme 1, lower part). As a side product, $(i\text{-Pr})_2P\text{-}(CH_2)_6\text{-}P(i\text{-Pr})_2$ is formed resulting from a metal halogen exchange in $Cl\text{-}(CH_2)_3\text{-}P(i\text{-Pr})_2$ followed by reaction with a second molecule $Cl(CH_2)_3\text{-}P(i\text{-Pr})_2$.

Spectroscopic data of **4a–g** (Table1; Experimental) are in agreement with their constitution. The $AX_3$ spin systems of the diastereotopic methyl groups in **4a–d** (also in **6a**, **7a**, and **9**) are not resolved in $CDCl_3$ solution. To verify the $J_{H,H}$ and the $J_{H,P}$ coupling constants, $^1H$ NMR spectra were also acquired in $C_6D_6$ solution.

As expected, the phenyl substituted phosphines **4e–g** are moderately stable after purification. The diisopropylphosphino derivatives **4a–d** undergo fast decomposition when exposed to air.

**1** is also suitable to allow elegant access to potential terdentate ligands. In analogy to *Pignolet* and coworkers [15], stepwise metalation of **1** and reaction with $(i\text{-Pr})_2P\text{-Cl}$ or $Ph_2P\text{-Cl}$ yield P,N ligands **6a** and **6b** [14] and then the symmetrical P,P,N ligands **7a** and **7b** (Scheme 3) [15]. When metalation of **1** is performed with LDA instead of *n*-BuLi, secondary reaction with $Ph_2PCl$ affords $Ph_2P\text{-}N(i\text{-Pr})_2$ [16]. In **7a**, there are two diastereotopic $P(i\text{-Pr})_2$ groups, resulting in a magnetic inequivalence of the CH groups bound to each phosphorus and a duplication of the $CH_3$ signals in the $^1H$ and $^{13}C$ NMR spectra.

Analogous to the synthesis of 2,6-*bis*-(diphenylphosphino-methyl)-pyridine **10**, [17, 18], the diisopropylphosphino derivative **9** is accessible *via* reaction of 2,6-




**Scheme 3.** Synthesis of P,P,N ligands (*R*: *i*-Pr for **6a**, **7a**; Ph for **6b**, **7b**)

*bis*(chloromethyl)-pyridine **8** with $(i\text{-Pr})_2$PLi. **9** is expected to form highly stable chelate complexes.

Investigations on the coordination behaviour of these new hemilabile ligands and, in particular, details on their application to catalysis will be reported separately.

## Experimental

All manipulations were carried out under an atmosphere of dry argon by standard *Schlenk* techniques. Solvents were distilled prior to use after purification with standard methods. Commercially available reagents were used as received or freshly degassed. **6b** [14], **7b** [15], **10** [17], and Cl-$(CH_2)_3$-$(i\text{-Pr})_2$ [2] were prepared according to literature methods.

### *Physical measurements*

NMR spectra were acquired on a Bruker AC 200 spectrometer ($^1$H: 200.13 MHz, $^{13}$C: 50.32 MHz, $^{31}$P: 81.02 MHz) at 298 K. Chemical shifts are referenced to internal or external *TMS* ($^1$H, $^{13}$C) or to external 85% $H_3PO_4$ ($^{31}$P). In experiments using non-deuterated solvents, a coaxial tube with $D_2O$ serving as lock substance was inserted. Assignments were confirmed by $^1$H,$^1$H-COSY, $^1$H,$^{13}$C-HETCOR, $^{13}$C-DEPT, and selective $^{31}$P decoupling of $^1$H and $^{13}$C{$^1$H} NMR spectra. Coupling constants are given in Hz.

The kinetic measurement for the reaction of **3a** to **5a** was performed with a 0.1745 mol · dm$^{-3}$ $CDCl_3$ solution of **3a** and hexaethyldisiloxane (0.1712 mol · dm$^{-3}$) as an internal standard; $^1$H NMR spectra were acquired at 298 K every 15 min until nearly complete conversion of **2a**.

Mass spectra (EI: 70 eV, CI: $H_2O$, FAB: glycerine) were recorded on a Finigan SSQ 710 instrument. For GC-MS analysis, a Hewlett Packard 5890/5972 (He, 30 m HP5-MS capillary column) system was used. IR measurements were performed on a Perkin Elmer PC-16 spectrometer. The results of the elemental analyses agreed satisfactorily with the theoretical values.

### *General procedure for the synthesis of 2-(ω-chloroalkyl)pyridines*

2-Picoline is added dropwise to a freshly prepared solution of one equivalent *LDA* in *THF* at −50°C. After stirring for 3 h at room temperature, the dark red solution of lithiated picoline is transferred *via* a canula to a well-stirred solution of α-bromo-ω-chloro-*n*-alkane in thf (2cm$^3$ per 1 mmol) at

$-50°C$[a]. The mixture is stirred for 36 h at room temperature to complete reaction. After distillation of the solvent the residue is hydrolyzed with water (1 $cm^3$ per 1 mmol). The organic layer is separated, and the aqueous phase is extracted four times with diethyl ether. The combined organic phases are dried over $Na_2SO_4$, and the solvent is removed under vacuum. Fractionation on a 20 cm *Vigreux* column affords the products as light yellow viscous liquids.

*2-(4-Chlorobutyl)-pyridine, (***3a**; $C_9H_{12}ClN$)

Following the procedure described above, reaction of 4.66 g (50 mmol) **1** and 7.87 g (50 mmol) 1-bromo-3-chloro-propane affords the crude product which is dissolved in 10 $cm^3$ pentane, filtered over silica, and dried under vacuum to give 1.27 g (7.5 mmol, 15%) of **2a** (b.p.: 58°C at $4 \cdot 10^{-6}$ mbar). Pure **3a** slowly decomposes at $-78°C$.

$^1$H NMR ($CDCl_3$): $\delta = 8.51$ (d, $^3J = 4.6$, 1H, H-6), 7.58 (dt, $^3J = 7.6$, $^4J = 1.9$, 1H, H-4), 7.10 (m, 2H, H-3/5), 3.54 (t, $^3J = 6.2$, 2H, H-10), 2.80 (t, $^3J = 7.3$, 2H, H-7), 1.85 (m, 4H, H-8/9) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 161.4$ (C-2), 149.2 (C-6), 136.2 (C-4), 122.6 (C-3), 121.0 (C-5), 44.7 (C-10), 37.3 (C-7), 32.0 (C-9), 26.8 (C-8) ppm.

*2-(5-Chloropentyl)-pyridine* (**3b**; $C_{10}H_{14}ClN$)

Reaction of 5.59 g (60 mmol) **1** and 10.29 g (60 mmol) 1-bromo-4-chloro-butane affords 7.97 g (43 mmol, 72%) of **2b** (b.p.: 72°C at 0.01 mbar), which is stable at $-30°C$.

$^1$H NMR ($CDCl_3$): $\delta = 8.50$ (ddd, $^3J = 4.9$, $^4J = 1.9$, $^5J = 1.0$, 1H, H-6), 7.55 (dt, $^3J = 7.7$, $^4J = 1.9$, 1H, H-4), 7.08 (m, 2H, H-3/5), 3.50 (t, $^3J = 6.6$, 2H, H-11), 2.77 (t, $^3J = 7.6$, 2H, H-7), 1.76 (m, 4H, H-8/10), 1.47 (m, 2H, H-9) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 161.9$ (C-2), 149.2 (C-6), 136.2 (C-4), 122.7 (C-3), 120.9 (C-5), 44.9 (C-11), 38.1 (C-7), 32.4 (C-10), 29.0 (C-8), 26.6 (C-9) ppm; MS (EI): *m/z* (%) = 182 (0.3), 148, 134, 120, 106, 93 (100), 78, 65, 51.

*2-(6-Chlorohexyl)-pyridine* (**3c**; $C_{11}H_{16}ClN$)

Reaction of 9.31 g (0.1 mol) **1** and 18.55 g (0.1 mol) 1-bromo-5-chloro-pentane affords 13.41 g (68 mmol, 68%) of **2c** (b.p.: 88°C at $1 \cdot 10^{-5}$ mbar).

$^1$H NMR ($CDCl_3$): $\delta = 8.47$ (ddd, $^3J = 4.9$, $^4J = 1.8$, $^5J = 1.0$, 1H, H-6), 7.52 (dt, $^3J = 7.6$, $^4J = 1.9$, 1H, H-4), 7.08 (d, $^3J = 7.7$, 1H, H-3), 7.03 (ddd, $^3J = 7.5$, $^4J = 4.9$, $^5J = 1.2$, 1H, H-5), 3.46 (t, $^3J = 6.7$, 2H, H-12), 2.74 (t, $^3J = 7.7$, 2H, H-7), 1.71 (m, 4H, H-8/11), 1.38 (m, 4H, H-9/10) ppm; $^{13}$C NMR ($CDCl_3$): $\delta =$ 162.1 (C-2), 149.1 (C-6), 136.1 (C-4), 122.6 (C-3), 120.8 (C-5), 44.9 (C-12), 38.1 (C-7), 32.4 and 29.5 (C-8/11), 28.4 and 26.6 (C-9/10) ppm; MS (EI): *m/z* (%) = 196 (0.3), 162, 148, 134, 120, 106, 93 (100), 78, 65, 51.

*2-(7-Chloroheptyl)-pyridine* (**3d**; $C_{12}H_{18}ClN$)

Reaction of 9.31 g (0.1 mol) **1** and 19.95 g (0.1 mol) 1-bromo-6-chloro-hexane affords 16.97 g (80 mmol, 80%) **2d** (bp.: 82°C at $1 \cdot 10^{-5}$ mbar).

$^1$H NMR ($CDCl_3$): $\delta = 8.48$ (ddd, $^3J = 4.8$, $^4J = 1.8$, $^5J = 0.9$, 1H, H-6), 7.53 (dt, $^3J = 7.6$, $^4J = 1.9$, 1H, H-4), 7.09 (d, $^3J = 7.7$, 1H, H-3), 7.05 (ddd, $^3J = 7.5$, $^4J = 5.0$, $^5J = 1.2$, 1H, H-5), 3.47 (t, $^3J = 6.7$, 2H, H-13), 2.74 (t, $^3J = 7.7$, 2H, H-7), 1.71 (m, 4H, H-8/11), 1.38 (m, 6H, H-9/10/12) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.3$ (C-2), 149.2 (C-6), 136.1 (C-4), 122.6 (C-3), 120.8 (C-5), 45.0 (C-13), 38.3 (C-7), 32.5, 29.7 and 29.1 (C-8/11/12), 28.6 and 26.7 (C-9/10) ppm; MS (EI): *m/z* (%) = 210 (0.3), 176, 162, 148, 134, 120, 106, 93 (100), 78, 65, 51.

[a] Lithiation may be also carried out with *n*-BuLi solution

*1,2,3,4-Tetrahydroquinolizinium chloride* (**5a**; $C_9H_{12}ClN$)

Compound **3a**, kept at 25°C for several hours, affords crystalline colourless **5a** in quantitative yield. **5a** is washed with hexane, dried under vacuum, and has to be stored in a dry atmosphere due to its hygroscopic character.

$^1$H NMR ($CDCl_3$): $\delta = 9.61$ (dm, $^3J = 6.3$, 1H, H-6), 8.29 (dt, $^3J = 7.8$, $^4J = 1.4$, 1H, H-4), 7.89 (d, $^3J = 7.7$, 1H, H-3), 7.76 (t, $^3J = 6.9$, 1H, H-5), 4.91 (t, $^3J = 5.9$, 2H, H-7), 3.28 (t, $^3J = 6.6$, 2H, H-10), 2.07 (m, 2H, H-8), 1.97 (m, 2H, H-9) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 155.9$ (C-2), 145.7 (C-6), 144.3 (C-4), 128.6 (C-3), 125.2 (C-5), 55.6 (C-7), 28.4 (C-10), 21.0 (C-8), 17.3 (C-10) ppm; MS (FAB): *m/z* (%) = 303 (27), 226 (37), 185 (25), 134 (100).

*7,8,9,10-Tetrahydro-6H-pyrido[1,2-a]azepinium chloride* (**5b**; $C_{10}H_{14}ClN$)

Compound **3b**, reacted at 130°C for 2 h, gives crystalline colourless **5b** in quantitative yield. **5b** is washed with hexane, dried under vacuum, and has to be stored in a dry atmosphere.

$^1$H NMR ($CDCl_3$): $\delta = 9.74$ (dd, $^3J = 6.1$, $^4J = 1.3$, 1H, H-6), 8.32 (dt, $^3J = 7.8$, $^4J = 1.5$, 1H, H-4), 7.91 (dd, $^3J = 8.0$, $^4J = 1.5$, 1H, H-3), 7.75 (dd, $^3J = 7.7$, $^4J = 6.5$, $^5J = 1.5$, 1H, H-5), 5.06 (m, 2H, H-7), 3.30 (m, 2H, H-11), 1.74 (m, 6H, H-8/9/10) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 159.5$ (C-2), 146.7 (C-6), 145.5 (C-4), 129.0 (C-3), 125.9 (C-5), 61.1 (C-7), 34.1 (C-11), 28.1, 26.8, 24.5 (C-8/9/10) ppm; MS (EI): *m/z* (%) = 331 (2), 294 (23), 184 (24), 148 (31), 147 (80), 146 (22), 132 (19), 120 (36), 118 (55), 106 (21), 93 (100), 78 (17); MS (FAB): *m/z* (%) = 331 (10), 295 (2), 148 (100), 132 (6), 118 (7), 106 (7).

*General procedure for the synthesis of ω-2-pyridyl-n-alkylphosphines*

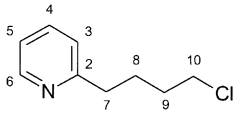
To a vigorously stirred solution of $(i\text{-Pr})_2$PH in *THF* (3 cm$^3$ per mmol), one equivalent MeLi (1.6 *N* solution in diethyl ether) or *n*-BuLi (1.6 *N* solution in hexane) is added at −30°C. The mixture is allowed to warm up slowly to 25°C and is stirred for another 3 h. The light yellow phosphide solution is now transferred dropwise to a stirred solution of the 2-(ω-chloroalkyl)pyridine in *THF* (2 cm$^3$ per mmol) at −50°C. The mixture is reacted for 12 h at 25°C. Volatile components are removed carefully at reduced pressure. The raw product is obtained from the residue by high vacuum condensation into a cold trap or by crystallization. Further purification is performed by vacuum distillation or recrystallization.

*2-(4-Diisopropylphosphino-butyl)-pyridine* (**4a**; $C_{15}H_{26}NP$)

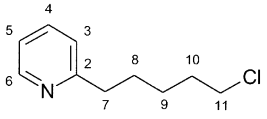
Method 1: Analogous to the general procedure, 15.8 cm$^3$ (25 mmol) MeLi, 2.99 g (25 mmol) $(i\text{-Pr})_2$PH and 4.30 g (25 mmol) **3a** yield 3.69 g (15 mmol, 58%) **4a** after distillation (b.p.: 98°C at $4 \cdot 10^{-6}$ mbar) as a light yellow liquid.

Method 2: A solution of 20 mmol **2** in 30 cm$^3$ *THF* is prepared as described above. This solution is added dropwise to a solution of 3.89 g (20 mmol) Cl-$(CH_2)_3$-P$(i\text{-Pr})_2$ in 30 cm$^3$ *THF* at −60°C. After 90 min the reaction mixture is allowed to warm up to 25°C under stirring. The remaining red solution is refluxed for 4 h, hydrolyzed with 20 cm$^3$ water, and extracted with diethyl ether. The organic phase is dried over $Na_2SO_4$ and filtered. The solvent is removed under vacuum, and the residue is condensed into a cold trap to yield 1.63 g (6.5 mmol, 32%) **4a**.

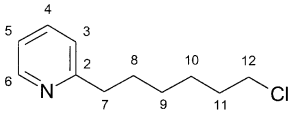
$^1$H NMR ($CDCl_3$): $\delta = 8.45$ (ddd, $^3J = 4.9$, $^4J = 1.8$, $^5J = 1.0$, 1H, H-6), 7.51 (dt, $^3J = 7.7$, $^4J = 1.9$, 1H, H-4), 7.07 (dt, $^3J = 7.8$, $^4J = 1.1$, 1H, H-3), 7.01 (ddd, $^3J = 7.5$, $^4J = 4.9$, $^5J = 1.2$, 1H, H-5), 2.74 (t, $^3J = 7.7$, 2H, H-7), 1.77 (m, 2H, H-8), 1.63 (dsp, $^3J = 7.1$, $^2J_{HP} = 2.8$, 2H, H-12), 1.48 (m, 2H, H-9), 1.32 (m, 2H, H-10), 1.00 (dd, $^3J = 7.2$, $^3J_{HP}$ =13.8, 6H, H-13a), 0.97 (dd, $^3J = 6.9$, $^3J_{HP} = 11.3$, 6H, H-13b) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.1$ (C-2), 149.1 (C-6), 136.1 (C-4), 122.5 (C-3), 120.7 (C-5), 38.0 (C-7), 31.6 (d, $|^3J_{CP}| = 11.8$, C-8), 27.9 (d, $|^2J_{CP}| = 18.7$, C-9), 23.1 (d,



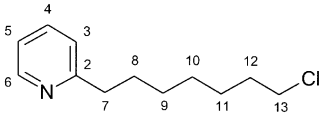
**3a**



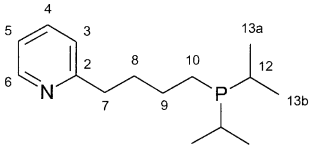
**3b**



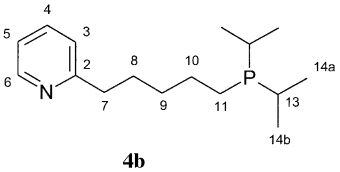
**3c**



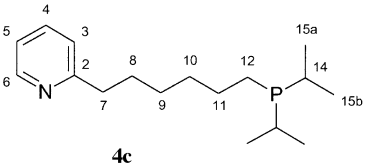
**3d**



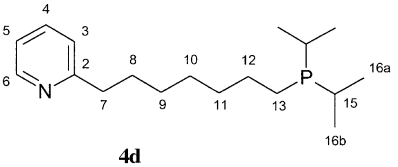
**4a**



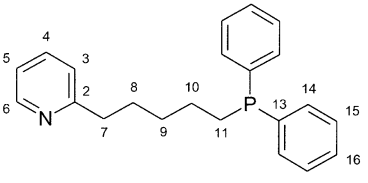
**4b**



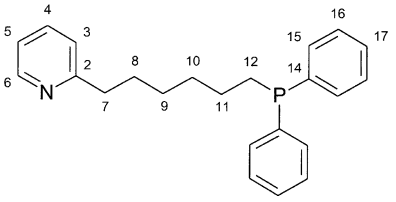
**4c**



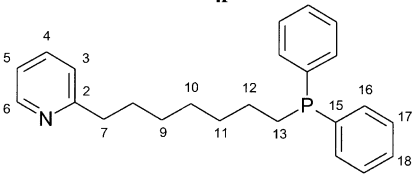
**4d**



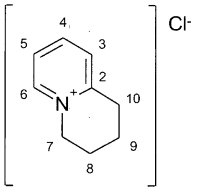
**4e**



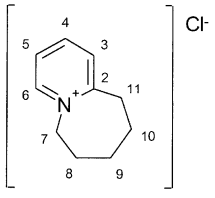
**4f**



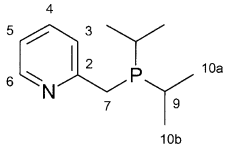
**4g**



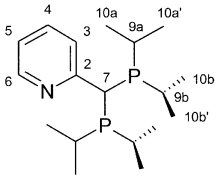
**5a**



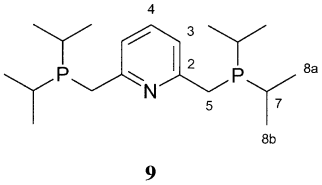
**5b**



**6a**



**7a**



**9**

$|^1J_{CP}| = 12.2$, C-12), 21.4 (d, $|^1J_{CP}| = 16.8$, C-10), 20.0 (d, $|^2J_{CP}| = 15.6$, C-13a), 18.7 (d, $|^2J_{CP}| = 9.2$, C-13b) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = 4.4$ ppm; MS (EI): *m/z* (%) = 251 (2), 236, 222, 208 (100), 166, 145, 132, 118, 106, 90, 76, 65, 51.

*2-(5-Diisopropylphosphino-pentyl)-pyridine* (**4b**; $C_{16}H_{28}NP$)

Analogous to the procedure described above, 21.9 $cm^3$ (35 mmol) MeLi, 4.14 g (35 mmol) $(i\text{-Pr})_2PH$, and 6.43 g (35 mmol) **3b** yield 7.76 g (29 mmol, 84%) **4b** after distillation (b.p.: 90°C at $4 \cdot 10^{-6}$ mbar) as a colourless liquid.

$^1$H NMR ($CDCl_3$): $\delta = 8.50$ (ddd, $^3J = 4.8$, $^4J = 1.8$, $^5J = 1.0$, 1H, H-6), 7.55 (dt, $^3J = 7.7$, $^4J = 1.9$, 1H, H-4), 7.08 (m, 2H, H-3/5), 2.76 (t, $^3J = 7.8$, 2H, H-7), 1.71 (m, 2H, H-8), 1.67 (dsp, $^3J = 7.0$, $^2J_{HP} = 2.9$, 2H, H-13), 1.39–1.52 (m, 4H, H-9/10), 1.24–1.38 (m, 2H, H-11), 1.04 (dd, $^3J = 7.2$, $^3J_{HP} = 13.8$, 6H, H-14a), 1.02 (dd, $^3J = 7.0$, $^3J_{HP} = 11.1$, 6H, H-14b) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.2$ (C-2), 149.0 (C-6), 136.0 (C-4), 122.5 (C-3), 120.7 (C-5), 38.2 (C-7), 31.2 (d, $|^3J_{CP}| = 11.8$, C-9), 29.5 (C-8), 27.9 (d, $|^2J_{CP}| = 18.3$, C-10), 23.1 (d, $|^1J_{CP}| = 12.2$, C-13), 21.4 (d, $|^1J_{CP}| = 16.4$, C-11), 20.0 (d, $|^2J_{CP}| = 15.3$, C-14a), 18.7 (d, $|^2J_{CP}| = 9.2$, C-14b) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = 4.4$ ppm; MS (EI): *m/z* (%) = 265 (13), 250, 222, 180, 173 (100), 160, 148, 132, 118, 106, 90, 76, 65, 43.

*2-(6-Diisopropylphosphino-hexyl)-pyridine* (**4c**; $C_{17}H_{30}NP$)

21.9 $cm^3$ (35 mmol) MeLi, 4.14 g (35 mmol) $(i\text{-Pr})_2PH$, and 6.92 g (35 mmol) **3c** yield 8.75 g (31 mmol, 89%) **4c** after condensation at $4 \cdot 10^{-6}$ mbar into a cold trap as a colourless liquid.

$^1$H NMR ($CDCl_3$): $\delta = 8.49$ (ddd, $^3J = 4.9$, $^4J = 1.8$, $^5J = 0.9$, 1H, H-6), 7.55 (dt, $^3J = 7.6$, $^4J = 1.9$, 1H, H-4), 7.10 (d, $^3J = 7.5$, 1H, H-3), 7.05 (ddd, $^3J = 7.4$, $^4J = 4.8$, $^5J = 1.2$, 1H, H-5), 2.76 (t, $^3J = 7.7$, 2H, H-7), 1.71 (m, 2H, H-8), 1.67 (dsp, $^3J = 7.1$, $^2J_{HP} = 2.8$, 2H, H-14), 1.20–1.50 (m, 8H, H-9/10/11/12), 1.04 (dd, $^3J = 7.2$, $^3J_{HP} = 13.9$, 6H, H-15a), 1.01 (dd, $^3J = 6.9$, $^3J_{HP} = 11.1$, 6H, H-15b) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.4$ (C-2), 149.2 (C-6), 136.1 (C-4), 122.6 (C-3), 120.8 (C-5), 38.4 (C-7), 31.4 (d, $|^3J_{CP}| = 11.4$, C-10), 29.8 and 29.1 (C-8/9), 28.1 (d, $|^2J_{CP}| = 18.3$, C-11), 23.2 (d, $|^1J_{CP}| = 12.2$, C-14), 21.6 (d, $|^1J_{CP}| = 16.4$, C-12), 20.1 (d, $|^2J_{CP}| = 15.6$, C-15a), 18.8 (d, $|^2J_{CP}| = 9.5$, C-15b) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = 4.5$ ppm; MS (EI): *m/z* (%) = 279 (22), 264, 236, 194, 187 (100), 173, 162, 145, 132, 118, 106, 93, 90, 76, 65, 43.

*2-(7-Diisopropylphosphino-heptyl)-pyridine* (**4d**; $C_{18}H_{32}NP$)

21.9 $cm^3$ (35 mmol) MeLi, 4.14 g (35 mmol) $(i\text{-Pr})_2PH$, and 7.41 g (35 mmol) **3d** yield 6.93 g (24 mmol, 67%) **4d** after distillation (b.p.: 124°C at $2 \cdot 10^{-4}$ mbar) as a colourless liquid.

$^1$H NMR ($CDCl_3$): $\delta = 8.48$ (ddd, $^3J = 4.9$, $^4J = 1.8$, $^5J = 1.0$, 1H, H-6), 7.53 (dt, $^3J = 7.7$, $^4J = 1.9$, 1H, H-4), 7.09 (d, $^3J = 7.7$, 1H, H-3), 7.04 (ddd, $^3J = 7.5$, $^4J = 5.0$, $^5J = 1.2$, 1H, H-5), 2.74 (t, $^3J = 7.8$, 2H, H-7), 1.69 (m, 2H, H-8), 1.66 (dsp, $^3J = 7.1$, $^2J_{HP} = 2.8$, 2H, H-15), 1.24–1.45 (m, 10H, H-9/10/11/12/13), 1.03 (dd, $^3J = 7.2$, $^3J_{HP} = 13.8$, 6H, H-16a), 1.00 (dd, $^3J = 7.0$, $^3J_{HP} = 11.6$, 6H, H-16b) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.4$ (C-2), 149.1 (C-6), 136.1 (C-4), 122.6 (C-3), 120.8 (C-5), 38.4 (C-7), 31.4 (d, $|^3J_{CP}| = 11.4$, C-11), 29.8 (C-8), 29.24 and 29.15 (C-9/10), 28.1 (d, $|^2J_{CP}| = 17.9$, C-12), 23.2 (d, $|^1J_{CP}| = 11.8$, C-15), 21.5 (d, $|^1J_{CP}| = 16.8$, C-13), 20.1 (d, $|^2J_{CP}| = 15.6$, C-16a), 18.8 (d, $|^2J_{CP}| = 9.1$, C-16b) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = 4.4$ ppm; MS (EI): *m/z* (%) = 293 (14), 278, 250, 201, 187, 176, 162, 145, 132, 118, 106, 93, 90 (100), 76, 65, 61, 43.

*2-(5-Diphenylphosphino-pentyl)-pyridine* (**4e**; $C_{22}H_{24}NP$)

12.8 $cm^3$ (20 mmol) *n*-BuLi, 3.80 g (20 mmol) $Ph_2PH$, and 3.75 g (20 mmol) **3b** yield 4.92 g (15 mmol, 72%) **4e** after crystallization from hexane at −35°C as colourless crystals (m.p.: 44°C).

$^1$H NMR ($CDCl_3$): $\delta = 8.50$ (ddd, $^3J = 4.6$, $^4J = 1.9$, $^5J = 1.1$, 1H, H-6), 7.54 (dt, $^3J = 7.6$, $^4J = 1.9$, 1H, H-4), 7.40 (m, 4H, H-14), 7.31 (m, 6H, H-15/16), 7.08 (d, $^3J = 7.7$, 1H, H-3), 7.05 (dd, $^3J = 7.5$, $^5J = 1.3$, 1H, H-5), 2.74 (t, $^3J = 7.6$, 2H, H-7), 2.04 (m, 2H, H-11), 1.73 (m, 2H, H-8), 1.49 (m, 4H, H-9/10) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.2$ (C-2), 149.2 (C-6), 138.9 (d, $|^1J_{CP}| = 13.0$, C-13), 136.1 (C-4), 132.6 (d, $|^2J_{CP}| = 18.3$, C-14), 128.4 (C-16), 128.3 (d, $|^3J_{CP}| = 6.9$, C-15), 122.6 (C-3), 120.8 (C-5), 38.2 (C-7), 30.9 (d, $|^3J_{CP}| = 12.6$, C-9), 29.4 (C-8), 27.9 (d, $|^1J_{CP}| = 11.5$, C-11), 25.8 (d, $|^2J_{CP}| = 16.0$, C-10) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = -15.6$ ppm; MS (CI): *m/z* (%) = 334 (100), 255, 241, 199, 183, 148, 134, 108, 93.

*2-(6-Diphenylphosphino-hexyl)-pyridine* (**4f**; $C_{23}H_{26}NP$)

Analogous to the synthesis of **4c**, 18.4 cm$^3$ (29 mmol) *n*-BuLi, 5.47 g (29 mmol) $Ph_2PH$, and 5.81 g (29 mmol) **3c** yield 7.92 g (23 mmol, 78%) **4f** after crystallization from hexane at −35°C as colourless crystalline needles (m.p.: 48°C).

$^1$H NMR ($CDCl_3$): $\delta = 8.51$ (ddd, $^3J = 4.9$, $^4J = 1.8$, $^5J = 0.9$, 1H, H-6), 7.55 (dt, $^3J = 7.6$, $^4J = 1.8$, 1H, H-4), 7.28–7.44 (m, 10H, H-15/16/17), 7.07 (m, 2H, H-3/5), 2.75 (t, $^3J = 7.7$, 2H, H-7), 2.03 (m, 2H, H-12), 1.70 (m, 2H, H-8), 1.27–1.54 (m, 6H, H-9/10/11) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.3$ (C-2), 149.2 (C-6), 139.0 (d, $|^1J_{CP}| = 13.4$, C-14), 136.1 (C-4), 132.6 (d, $|^2J_{CP}| = 18.3$, C-15), 128.4 (C-17), 128.3 (d, $|^3J_{CP}| = 6.5$, C-16), 122.6 (C-3), 120.8 (C-5), 38.3 (C-7), 31.0 (d, $|^3J_{CP}| = 12.6$, C-10), 29.7 (C-8), 28.9 (C-9), 28.0 (d, $|^1J_{CP}| = 11.4$, C-12), 25.8 (d, $|^2J_{CP}| = 16.0$, C-11) ppm. $^{31}$P NMR ($CDCl_3$): $\delta = -15.5$ ppm; MS (CI): *m/z* (%) = 348 (100), 255, 241, 199, 187, 162, 148, 134, 109, 93.

*2-(7-Diphenylphosphino-heptyl)-pyridine* (**4g**; $C_{24}H_{28}NP$)

Analogous to the synthesis of **4e**, 18.8 cm$^3$ (30 mmol) *n*-BuLi, 5.59 g (30 mmol) $Ph_2PH$, and 6.35 g (30 mmol) **3d** yield 8.60 g (24 mmol, 79%) **4g** after crystallization from hexane at −35°C as colourless crystalline needles (m.p:. 30°C).

$^1$H NMR ($CDCl_3$): $\delta = 8.51$ (ddd, $^3J = 4.9$, $^4J = 1.5$, $^5J = 0.9$, 1H, H-6), 7.54 (dt, $^3J = 7.6$, $^4J = 1.9$, 1H, H-4), 7.28–7.46 (m, 10H, H-16/17/18), 7.07 (m, 2H, H-3/5), 2.76 (t, $^3J = 7.8$, 2H, H-7), 2.03 (m, 2H, H-13), 1.71 (m, 2H, H-8), 1.38 (m, 8H, H-9/10/11/12) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 162.4$ (C-2), 149.1 (C-6), 139.0 (d, $|^1J_{CP}| = 13.0$, C-15), 136.1 (C-4), 132.6 (d, $|^2J_{CP}| = 18.3$, C-16), 128.33 (C-18), 128.27 (d, $|^3J_{CP}| = 6.9$, C-17), 122.5 (C-3), 120.7 (C-5), 38.3 (C-7), 31.0 (d, $|^3J_{CP}| = 13.0$, C-11), 29.7 (C-8), 29.1 and 29.0 (C-9/10), 27.9 (d, $|^1J_{CP}| = 11.1$, C-13), 25.8 (d, $|^2J_{CP}| = 16.0$, C-12) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = -15.5$ ppm; MS (CI): *m/z* (%) = 362 (100), 284, 269, 255, 176, 109, 93.

*2-(Diisopropylphosphino-methyl)-pyridine* (**6a**; $C_{12}H_{20}NP$)

A solution of 2.33 g (25 mmol) **1** in 50 cm$^3$ *THF* is treated with one equivalent *n*-BuLi at −50°C. The mixture is stirred for one hour at 25°C to give a clear red solution of **2** which is slowly transferred to a well stirred solution of 3.82 g (25 mmol) $(i\text{-Pr})_2PCl$ in 50 cm$^3$ *THF* at −50°C. After the reaction mixture has been stirred for 12 h, the volatile components are removed carefully at reduced pressure. 4.05 g (19 mmol, 77%) **6a** are obtained as a yellow liquid from the residue by distillation (b.p.: 68°C at $4 \cdot 10^{-6}$ mbar).

$^1$H NMR ($CDCl_3$): $\delta = 8.41$ (ddd, $^3J = 4.9$, $^4J = 1.8$, $^5J = 0.9$, 1H, H-6), 7.49 (dt, $^3J = 7.6$, $^4J = 1.9$, 1H, H-4), 7.24 (ddt, $^3J = 7.9$, $^5J = 0.9$, $^4J_{HP} = 0.8$, 1H, H-3), 6.99 (ddd, $^3J = 7.4$, $^4J = 5.0$, $^5J = 1.2$, 1H, H-5), 2.94 (d, $^2J_{HP} = 2.2$, 2H, H-7), 1.75 (dsp, $^3J = 7.1$, $^2J_{HP} = 1.9$, 2H, H-8), 1.00 (dd, $^3J = 7.0$, $^3J_{HP} = 11.5$, 6H, H-9a), 0.99 (dd, $^3J = 7.2$, $^3J_{HP} = 13.6$, 6H, H-9b) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 160.6$ (d, $|^4J_{CP}| = 8.4$, C-2), 149.0 (C-6), 135.9 (C-4), 123.5 (d, $|^3J_{CP}| = 6.9$, C-3), 120.5

(d, $|^5J_{CP}| = 1.5$, C-5), 32.3 (d, $|^1J_{CP}| = 22.1$, C-7), 23.4 (d, $|^1J_{CP}| = 13.7$, C-8), 19.6 (d, $|^2J_{CP}| = 14.5$, C-9a), 18.8 (d, $|^2J_{CP}| = 10.7$, C-9b), MS (EI): *m/z* (%) = 209 (2.4), 194, 166, 150, 135, 124 (100), 93, 78, 65.

*2-(bis-Diisopropylphosphino-methyl)-pyridine* (**7a**; $C_{18}H_{33}NP_2$)

Analogous to the synthesis of **6a**, 6.2 cm$^3$ (10 mmol) *n*-BuLi, 2.09 g (10 mmol) **6a** and 1.53 g (10 mmol) $(i\text{-Pr})_2$PCl yield 1.68 g (5 mmol, 52%) **7a** as a light brown viscous liquid (b.p.: 108°C at $3 \cdot 10^{-6}$ mbar).

$^1$H NMR ($CDCl_3$): $\delta = 8.42$ (ddd, $^3J = 4.8$, $^4J = 1.9$, $^5J = 0.9$, 1H, H-6), 7.47 (dt, $^3J = 7.7$, $^4J = 1.9$, 1H, H-4), 7.13 (ddt, $^3J = 7.9$, $^5J = 1.0$, $^4J_{HP} = 0.3$, 1H, H-3), 6.97 (ddd, $^3J = 7.4$, $^4J = 4.8$, $^5J = 1.2$, 1H, H-5), 3.51 (s, 1H, H-7), 2.00 (tsp, $^3J = 7.1$, $^2J_{HP} = 1.8$, 2H, H-9a), 1.87 (tsp, $^3J = 7.2$, $^2J_{HP} = 1.5$, 2H, H-9b), 1.17 (dt, $^3J = 7.2$, $^3J_{HP} = 13.2$, 6H, H-10a), 1.08 (dt, $^3J = 7.0$, $^3J_{HP} = 12.4$, 6H, H-10a′), 0.97 (dt, $^3J = 7.4$, $^3J_{HP} = 15.1$, 6H, H-10b), 0.63 (dt, $^3J = 7.2$, $^3J_{HP} = 10.3$, 6H, H-10b′) ppm; $^{13}$C NMR ($CDCl_3$): 160.2 (t, $|^2J_{CP}| = 2.7$, C-2), 148.9 (C-6), 135.3 (C-4), 123.6 (t, $|^3J_{CP}| = 3.8$, C-3), 120.3 (C-5), 38.4 (t, $|^1J_{CP}| = 33.9$, C-7), 22.2 (t, $|^2J_{CP}| = 10.7$, C-10b), 22.0 (t, $|^1J_{CP}| = 5.0$, C-9a), 21.8 (t, $|^1J_{CP}| = 6.9$, C-9b), 20.5 (t, $|^2J_{CP}| = 8.4$, C-10a), 20.0 (t, $|^2J_{CP}| = 8.0$, C-10a′), 19.3 (t, $|^2J_{CP}| = 3.8$, C-10b′) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = 12.6$ ppm; MS (CI): *m/z* (%) = 326 (100), 282, 251, 226, 210, 196, 166, 135, 124, 93.

*2,6-bis-(Diisopropylphosphino-methyl)-pyridine* (**9**; $C_{19}H_{35}NP$)

A solution of 2.62 g (22 mmol) $(i\text{-Pr})_2$PH in 20 cm$^3$ *THF* is treated with one equivalent *n*-BuLi at −50°C. The mixture is stirred for 3 h without further cooling to yield a yellow phosphide solution. This solution is slowly transferred to a stirred solution of 1.96 g (11 mmol) 2,6-bis(chloromethyl)-pyridine (**8**) in 30 ml *THF* at −50°C. After the reaction mixture has been stirred for 12 h, the volatile components are removed carefully at reduced pressure. 2.29 g (6.5 mmol, 59%) **6a** are obtained as a light yellow liquid from the residue by condensation into a cold trap at $4 \cdot 10^{-6}$ mbar.

$^1$H NMR ($CDCl_3$): $\delta = 7.40$ (dd, $^3J = 7.6$, 1H, H-4), 7.06 (d, $^3J = 7.5$, 2H, H-3), 2.91 (d, $^2J_{HP} = 2.2$, 2H, H-5), 1.76 (dsp, $^3J = 7.1$, $^2J_{HP} = 2.1$, 4H, H-7), 1.02 (dd, $^3J = 7.2$, $^3J_{HP} = 11.5$, 12H, H-8a), 1.01 (dd, $^3J = 7.2$, $^3J_{HP} = 13.5$, 12H, H-8b) ppm; $^{13}$C NMR ($CDCl_3$): $\delta = 159.7$ (d, $|^2J_{CP}| = 8.4$, C-2), 136.0 (C-4), 120.3 (dd, $|^3J_{CP}| = 8.0$, $|^5J_{CP}| = 1.9$, C-3), 32.4 (d, $|^1J_{CP}| = 21.4$, C-5), 23.4 (d, $|^1J_{CP}| = 13.7$, C-7), 19.6 (d, $|^2J_{CP}| = 14.5$, C-8b), 19.0 (d, $|^2J_{CP}| = 10.7$, C-8a) ppm; $^{31}$P NMR ($CDCl_3$): $\delta = 12.7$ ppm; MS (CI): *m/z* (%) = 340 (100), 296, 254, 240, 223, 135, 119.

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## References

[1] Jeffrey JC, Rauchfuss TB (1979) Inorg Chem **18**: 2658
[2] Pitter S, Dinjus E, Jung B, Görls H (1996) Z Naturforsch B **51b**: 934
[3] Pitter S, Dinjus E (1997) J Mol Cat A **125**: 39
[4] Newkome R (1993) Chem Rev **93**: 2067
[5] Drent E, Arnoldy P, Budzelaar PHM (1993) J Organomet Chem **455**: 247
[6] Chan WH, Zhang ZZ, Mak TCW, Che CM (1998) J Chem Soc Dalton Trans 797

[7] Budzelaar PHM (1998) J Org Chem **63**: 1131
[8] Chelucci G, Cabras MA, Botteghi C, Marchetti M (1994) Tetrahedron: Asymmetry **5**: 299
[9] Takashi H, Yoshio U, Hirofumi Y (1984) J Phys Chem **88**: 5150
[10] Moyhenan TM, Schofield K, Jones RAY, Katritzky AR (1962) J Chem Soc 2637
[11] Miyadera T, Kishada Y (1969) Tetrahedron **25**: 209
[12] Murphy JA, Sherburn MS (1991) Tetrahedron **47**: 4077
[13] Murphy JA, Dickinson JM (1990) J Chem Soc Chem Commun 439
[14] Alvarez M, Lugan N, Mathieu R (1994) J Chem Soc Dalton Trans 2755
[15] Anderson MP, Mattson BM, Pignolet LH (1983) Inorg Chem **22**: 2644
[16] Cristau H-J, Chene A, Christol H (1980) Synthesis **7**: 551
[17] Ziessel R (1989) Tetrahedron Lett **30**: 463
[18] Jiang Q, van Plew D, Murtuza S, Zhang X (1996) Tetrahedron Lett **6**: 797

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