Polyhedron 77 (2014) 10–16

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Benzazaphospholine-2-carboxylic acids: Synthesis, structure and properties of heterocyclic phosphanyl amino acids

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ARTICLE INFO

Article history:
Received 26 January 2014
Accepted 25 March 2014
Available online 13 April 2014

Keywords:
Phosphanes
Heterocycles
Ligands
Catalysis
Ethylene

ABSTRACT

1,3-Dialkyl-1,3-benzazaphospholine-2-carboxylic acids **2a**,**b** can be conveniently prepared by metalation and alkylation of *N*-methyl- and *N*-neopentyl-*o*-phosphanylaniline in liquid ammonia and cyclocondensation of the resulting *N*,*P*-disecondary phosphanylanilines **1a**,**b** with glyoxylic acid hydrate (GAH) in ether. The primary neopentylphosphanylaniline reacts with two equivalents of GAH and forms a phosphanyl-bis(amino acid) **3** with toluidine. α-Branched *P*-substituents induce strongly preferred formation of *trans*-diastereoisomers with *R*,*R*- and *S*,*S*-configuration at P and C2, as shown by a crystal structure analysis of **2a**, whereas a *P*-neopentyl (*P*-Np) group gives rise to *trans*/*cis*-diastereoisomeric mixtures. The *trans*-configuration exhibits the P lone-pair in *cis*-position to the COOH group, suitable for formation of five-membered chelate rings, as in diphenylphosphanylacetate nickel catalysts for ethylene oligomerization. Screening of **2a**,**b**/Ni(COD)$_2$ solutions in THF by a batch procedure indeed showed formation of catalysts for conversion of ethylene to linear oligomers and waxy low-molecular weight polymers. The conversion depends strongly on the size of the *N*-alkyl group, being slow and limited for the *N*-Me catalyst **2a**/**Ni** and much faster and more complete for the *N*-Np-substituted catalysts **2b**/**Ni** and **2c**/**Ni** (*N*-Np, *P*-*t*Bu). Comparison of **2b**/**Ni** with **2c**/**Ni** shows that the more bulky P-substituent further increases the catalyst activity.

1. Introduction

Recent studies on the synthesis of bulky *tert*-butyl-substituted heterocyclic phosphane ligands by addition of *tert*-butyllithium at the P=C bond of aromatic phosphorus heterocycles have included the discovery of a convenient route to 3-*tert*-butyl-1,3-benzazaphospholine-2-carboxylic acids [1]. These possess the same P-C-COOH structural unit as diphenylphosphanylacetic acid [2], which is used in the generation of nickel catalysts for the ethylene oligomerization in the SHOProcess [3], and also form highly active catalysts for this reaction. The amino function did not interfere with the catalytic conversion. This was observed also for various acyclic alkylamino- and arylamino-diphenylphosphanyl-acetic acids (phosphanylglycines) [4], whereas more closely related heterocyclic 3-phenyl-1,3-azaphospholidine-2-carboxylic acids (3-phenyl-phosphaprolines) without benzo-annulation required activation by sodium hydride to form active catalysts with Ni(COD)$_2$ [5]. To find out whether the higher activity of the benzazaphospholine-2-carboxylate-based nickel catalysts is attributable to the bulky *P*-*tert*-butyl substituent or to electronic effects of the intrinsic *o*-aminophenyl group, a preliminary study of the synthesis of less bulky *P*-alkyl-1,3-benzazaphospholine-2-carboxylic acids and their performance as ligands in the nickel catalyzed ethylene oligomerization was carried out.

2. Results and discussion

A well established strategy was chosen for the synthesis, namely the cyclocondensation of 2-phosphanyl-substituted amines, long since known for simple aldehydes and ketones [6]. Even the reaction of *o*-phosphanylaniline with pyruvic acid was reported to give 2-methyl-1,3-benzazaphospholine-2-carboxylic acid, but information on the properties and structure of this compound, except for the detection of a P–H absorption in the range 2240–2280 cm^{-1}, is not available [6c]. We used the condensation with glyoxylic acid hydrate (GAH). This acid proved sufficiently reactive at room temperature to undergo autocatalyzed

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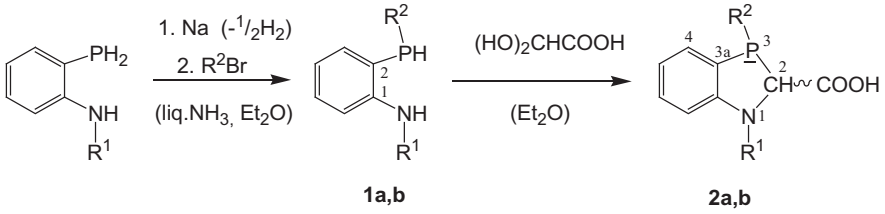
http://dx.doi.org/10.1016/j.poly.2014.03.046
0277-5387/

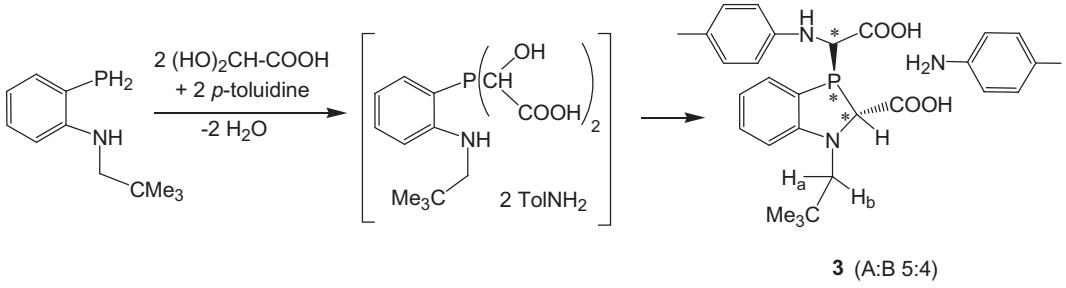
three-component one-pot condensations with secondary phosphanes and primary alkyl- or arylamines to phosphanylglycines [4] whereas aldehydes and ketones, including pyruvic and phenylglyoxyl acid, do not undergo analogous condensations. The starting phosphanes **1a**,**b** were prepared from *N*-methyl- and *N*-neopentyl-*o*-phosphanylaniline by *P*-alkylation. Attempts to achieve this via lithiation of the primary precursors with butyllithium in diethyl ether failed to give defined products, but metalation with sodium in liquid ammonia provided sufficiently reactive phosphides for preferred *P*-alkylation by isopropyl- and neopentylbromide, respectively. The reaction is regioselective but not regiospecific and also produced minor amounts of *N*-mono- and *P*-bisalkylated side products, which, because of their similar boiling points, are difficult to separate by distillation. For the subsequent cyclocondensation (Scheme 1) ethereal solutions of **1a**,**b** were added to GAH, dissolved in diethyl ether. The mixtures became turbid instantaneously, but clear again after some minutes. Small amounts of sticky precipitates were formed, identified as mixture of products and phosphine oxides. Most of the products **2a** and **2b** was still in the filtrate, and they were isolated by removal of ether as viscous oily mixtures, each consisting of two pairs of diastereoisomers. In **2a**, with a branched *P*-alkyl group and the small methyl group at nitrogen, the isomers with *trans*-configuration of the substituents in 2- and 3-position predominated (*trans:cis* ca. 9:1 by ^{1}H NMR integration) and allowed slow formation of a solid and finally crystallization, whereas **2b**, with neopentyl groups at both phosphorus and nitrogen, displayed a much lower *trans*/*cis*-isomer ratio (ca. 3:2) and remained oily. The ^{31}P NMR spectra of crude **2a** and **2b** also indicated small impurity signals (up to 10 mol%) in the region of $R_2PCH(OH)COOH$ species [7]. These are probably the primary condensation products and also formed in small equilibrium amounts by hydrolysis with traces of moisture, as demonstrated in more detail for acyclic α-phosphanyl amino acids [4]. Purification was possible by flash chromatography on silica gel using hexane/ethyl acetate (30% for **2a**, 2% for **2b**), but with a considerable loss of product by partial decomposition on reactive sites of silica gel in the column. In contrast to 1,3-benzazaphospholines without the COOH group, which were reported to be hydrolytically stable [6c], the carboxylic acid derivatives are sensitive to partial hydrolysis and attack by reactive OH species. The intrinsically Brønstedt acidic group may catalyze such reactions.

Reactions of *P*-primary *o*-phosphanylanilines with GAH are more complicated. Condensation of *N*-neopentyl-*o*-phosphanylaniline with GAH did not provide a defined product, either in a 1:1 or 1:2 M ratio. Only in the presence of *p*-toluidine (molar ratio 1:2:2) was a precipitate with defined composition obtained at room temperature (Scheme 2). According to the elemental analysis and NMR data it is a toluidinium salt (or hydrogen-bonded adduct with toluidine) of a phosphanylbis(amino acid) **3**, containing the benzazaphospholine and phosphanylglycine skeleton. Because of the rapid formation of phosphanylmono- and bis(glycolates) [7] and subsequent conversion with amines to phosphanylmono- or bis(glycines) [4] we assume primary reaction with two molecules of GAH, followed by cyclization and substitution of OH by the tolylamino group, rather than a stepwise reaction with GAH via an intermediate PH-functional benzazaphospholin-2-carboxylate.

Structural aspects. The structure elucidation of the new compounds is based on conclusive solution NMR data and for **2a** additionally on crystal structure analysis. Characteristic features of the phosphanes **1a** and **1b** are the PH doublets with one-bond P–H coupling constants of 214–217 Hz whereas the benzazaphospholine-2-carboxylic acids display typical doublets for the CH protons and carbon nuclei (Table 1). Small $^2J_{PH}$ coupling constants indicate *trans*-orientation of the P lone-pair and H-2, and therefore also *trans*-orientation of the *P*-substituent and the COOH group at C-2, which is strongly preferred in **2a** with its branched *P*-alkyl group and is the only form in the related 3-*tert*-butyl-1-neopentyl-benzazaphospholine-2-carboxylic acid (**2c**). The primary alkyl group at phosphorus in **2b**, despite the remote steric bulk of the *t*Bu-group in β-position, causes lower diastereoselectivity in the ring-closure step, with only moderate preference for *trans*- over *cis*-orientation (6:4). In compound **3** only *trans*-orientation of the *P*-substituent and 2-COOH is indicated, while the additional asymmetric carbon atom of the *P*-substituent gives rise to two pairs of diastereoisomers in a 5:4 ratio (by intensity of ^{31}P NMR signals). The $^1J_{PC}$ coupling constant is less indicative with respect to *cis*/*trans*-orientation, but proves the formation of the PCHN structural unit, and the chemical shift of this doublet allows us to distinguish



Scheme 1. Synthesis of **1a**,**b** and cyclocondensation with GAH to the heterocyclic phosphanyl amino acids **2a** (R^1 = Me, R^2 = *i*Pr) and **2b** (R^1, R^2 = neopentyl).



Scheme 2. Synthesis of the heterocyclic phosphanyl bis(amino acid) **3**.

Table 1
Characteristic NMR data of **2a**, **2b** and **3**, and comparison with those of **2c** (R^1 = Np, R^2 = *t*Bu) [1a] and *N*-*p*-tolyl-diphenylphosphanylglycine (TDPPG) [4b].

Compound; solvent	^{1}H NMR (PCH) δ ppm, (*J*, isomer)	^{13}C NMR (PCH) δ ppm, (*J*, isomer)	^{31}P NMR δ in ppm
2a (*trans*/*cis* ca. 9:1); [D_8]THF	4.33 (2.3 Hz, *E*) 4.32 (9.8 Hz, *Z*)	67.06 (23.9 Hz, *E*) n.d. (minor amount)	1.8 (*E*); −6.7 (*Z*),
2b (*trans*/*cis* ca. 6:4); CD_3OD	4.49 (2.6 Hz, *E*) 4.79 (17.0 Hz, *Z*)	71.37 (19.9 Hz, *E*); 68.66 (26.5 Hz, *Z*)	−17.3 (*E*); −18 (*Z*),
2c; CD_2Cl_2	4.54 (2.7 Hz, *E*)	67.39 (25.7 Hz)	19.5
3; [D_8]THF	4.25 (sh) 4.27 (br s) 4.73 (2.7 Hz) 4.98 (3.0 Hz)	68.44 (23.0 Hz) 68.52 (23.9 Hz) 57.33 (25.4 Hz) 57.39 (25.2 Hz)	−4.54; −6.10
TDPPG; [D_8]THF	4.73 (br s, superimp. by NH)	58.31 (17.6 Hz)	0.22

between acyclic and cyclic PCHN (more downfield shifted) moieties. For comparison the respective data of *N*-*p*-tolyl-diphenylphosphanylglycine (TDPPG) [4b] are included in Table 1. The phosphorus resonances were found in the region of tertiary phosphanes, display downfield shift with increasing branching of the *P*-alkyl group in the related compounds **2b** < **2a** < **2c**, as is typical for phosphanes [8] and show the number of diastereoisomers.

More detailed structure information gives the crystal structure analysis of **2a** (Figs. 1 and 2). Single crystals (space group $P\bar{1}$) were obtained from the dominating *trans*-diastereoisomers after flash chromatography by slow diffusion of hexane into the solution of **2a** in [D_8]THF. The unit cell contains two molecules with *2S*,*3S*- and *2R*,*3R*-configuration, respectively. The P–C3a bond is somewhat longer and the P–C2 bond considerably longer than in the benzazaphospholes, and the bond lengths are typical for P–C single bonds to sp^2 and sp^3-carbon, respectively. The N–C7A distance is still short in contrast to N–C2 or N–C8 and, together with the sum of C–N–C angles, indicates sp^2 hybridization at nitrogen and conjugation with the benzene π-system. The *trans*-configuration offers ideal conditions for formation of P^O$^-$-chelate complexes, as the *P* lone-pair is on the same side as the COOH group.

Tests for formation of ethylene oligomerization catalysts. The coordination behaviour towards transition metals was not studied during this preliminary investigation of benzazaphospholine-2-carboxylic acids, but the *in situ* generation of nickel catalysts for ethylene oligomerization was tested for **2a** and **2b** in order to evaluate the impact of the substituents at phosphorus and nitrogen compared to those in *P*-*tert*-butyl- benzazaphospholine-2-carboxylic acids with *N*-neopentyl (**2c**) [1a] and *N*-(1-arylethyl) substituents (aryl = *p*-anisyl, phenyl) [1b]. The screening was carried out with precatalysts, formed from pure *trans*-**2a** and the *trans*/*cis*-mixture of **2b**, respectively, with Ni(COD)$_2$ in THF, using a batch procedure and reaction monitoring by pressure/time registration (Fig. 3). After pressurizing the autoclave was heated up, at first to 70 °C (within 15–20 min). Whereas **2c** (Fig. 3, plot c) and the two recently tested 1-(aryl)ethyl-substituted *P*-*tert*-butyl-benzazaphospholine-2-carboxylic acids formed highly active catalysts

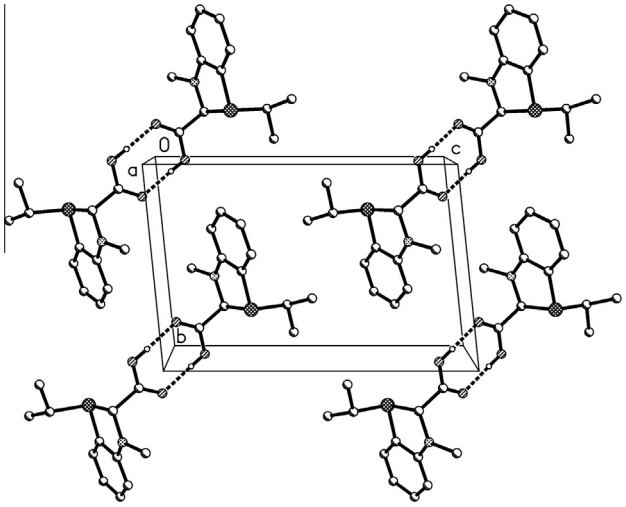


Fig. 2. Packing of dimers of **2a** in the crystal. Hydrogen bond: O2–H02 0.87(2), H02···O1#1 1.77(2), O2···O1#1 2.6397(12) Å, O2–H02···177.9(19)°.

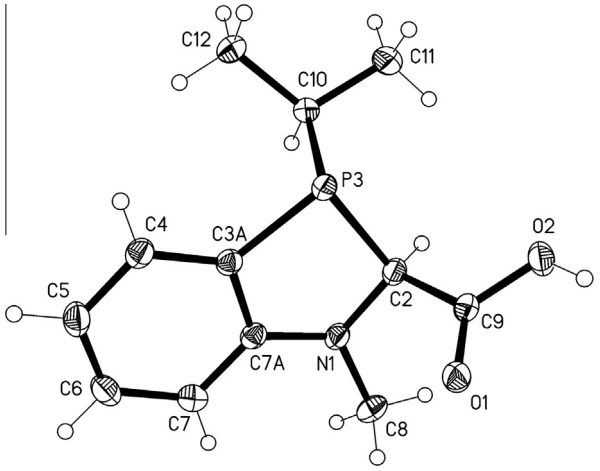


Fig. 1. Structure of the *2S*,*3S* enantiomer of racemic **2a** in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): P3–C3A 1.8159(12), C2–P3 1.8974(12), P3–C10 1.8629(12), N1–C7A 1.3790(15), N1–C2 1.4458(15), N1–C8 1.4550(15); C3A–P3–C2 89.08(5), N1–C2–P3 107.44(7), C7A–N1–C2 115.31(9); Σ(C–N–C) 356.9(9), Σ (C–P–C) 292.76(5).

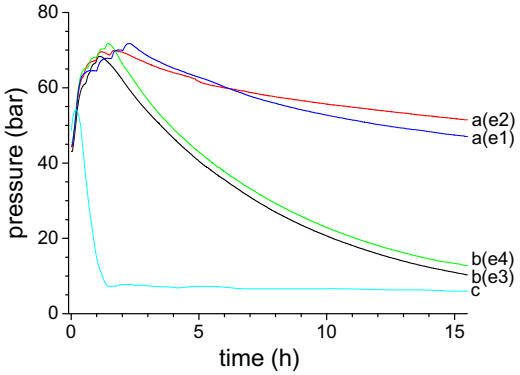


Fig. 3. Pressure–time plots for batch polymerization of ethylene with a) **2a**/Ni(COD)$_2$ (entries 1, 2), (b) **2b**/Ni(COD)$_2$ (entries 3, 4) in THF at 100 °C and (c) comparison with the *P*-*tert*-butyl-substituted *trans*-**2c**/Ni(COD)$_2$ in THF at 70 °C [1a].

Table 2
Oligomerization of ethylene with catalysts formed from **2a**,**b**[a].

N	Catalyst (μmol)	C_2H_4 g (mol), conv. g (%), TON (mol/mol)	Polymer (g),[b] mp. (°C), D (g/cm^3)[c]	Polymer: M_{NMR}[d] ($g\ mol^{-1}$), α-olefin (%), Me/C=C	Linear α-olefines C_6, C_8, C_{10}, C_{12}, C_{14}[e]
1	**2a** (93), $Ni(COD)_2$ (182)	16.4 (0.58), 8.8 (54), 3373	11.6, 107–112, -	M_{NMR} 600, 86, 1.4	13, 23, 21, 17, 6
2	**2a** (76), $Ni(COD)_2$ (84)	16.6 (0.59), 8.4 (51), 3940	-, -, -	n.d.	11, 12, 8, 5, 3
3	**2b** (81), $Ni(COD)_2$ (89)	16.9 (0.60), 15.8 (93), 6953	6.8, 108–114, 0.939	M_{NMR} 510, 91, 1.3	33, 28, 10, 2, 0.2
4	**2b** (78), $Ni(COD)_2$ (86)	14.7 (0.53), 14.1 (96), 6444	-, -, -	n.d.	30, 29, 12, 4, 0.6

[a] Batch oligo/polymerization of ethylene in THF, p_{start} of C_2H_4 at r.t. ca. 45 bar, begin of conversion at ca. 100 °C.
[b] Solid residue after flash distillation of volatiles, treatment with MeOH/aqueous conc. HCl (1:1), washing with MeOH and drying in a vacuum.
[c] Density of tablets of the solid (pressed at 10 kbar) determined by the sinking method in H_2O/EtOH.
[d] M_{NMR} based on ^1H NMR integrals of CH_2 and CH_3 vs. =CH protons in swollen polymers at 100 °C.
[e] GC peak area% of α-olefins in the flash distillate (1-butene not indicated by partial evaporation).

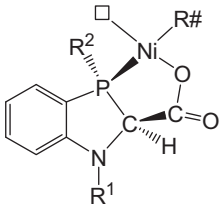


Fig. 4. Assumed catalyst species (R# = H or growing chain, □ = ethylene coordination site).

under these conditions (*p*/*t*-plots see Ref. [1b]), the **2a**/**Ni** and **2b**/**Ni** precatalysts remained still inactive. Catalysts were formed only at 100 °C , and the conversion of ethylene was much slower than in the catalysis by **2c**/**Ni** and incomplete for the **2a**/**Ni** catalyst (Table 2). Repeated experiments showed good reproducibility of the ethylene conversion and only marginal influence of excess $Ni(COD)_2$ used in one conversion with **2a**/**Ni** (entry 1).

Low molecular weight waxy polymers and liquid oligomers were formed. The selectivity of the **2a**/**Ni** and **2b**/**Ni** catalysts for strongly preferred formation of linear α-olefin oligo- and polymers (Table 2) is the same as for phosphanylacetate, -benzoate, -enolate or -phenolate nickel catalysts. This suggests that the mechanism is the same as demonstrated for the former types in more detail, involving formation of organonickel(II) P^O$^-$ chelate complexes (Fig. 4) and generation of NiH starting species in the initiation and chain-terminating β-hydride elimination [3].

The slow and rather incomplete conversion of ethylene in the presence of **2a**/**Ni** indicates that the substituent at nitrogen has a decisive impact on the performance of the benzazaphospholine-2-carboxylate nickel catalysts. A sufficiently bulky *N*-substituent is necessary to achieve high ethylene conversion, probably by sterically hindered coordination of the amino group at nickel. The size of the alkyl group at phosphorus is less important for the total conversion but affects the activation temperature and the conversion rate. As only the *trans*-diastereoisomers of **2b** can form P^O$^-$ nickel chelate complexes, the lower activity of **2b**/**Ni** compared to **2c**/**Ni** and *N*-(1-arylethyl)-benzazaphospholine-2-carboxylate nickel catalysts [1] can be attributed in part to the presence of *cis*-diastereoisomers of **2b**. The very marked decrease of the reaction rate and shorter polymer chains compared to the results of catalysis with *trans*-**2c**/**Ni**, however, is accounted for also by interfering side reactions, which are allowed directly by the primary, β-branched *P*-neopentyl group or indirectly by the sterically possible occurrence of the *cis*-diastereoisomeric ligand with other coordination properties.

3. Conclusions

1,3-Benzazaphospholine-2-carboxylic acids can be synthesized from *N*,*P*-disecondary *o*-phosphanylanilines, accessible via metalation and subsequent alkylation of *P*-primary *o*-phosphanylanilines in liquid ammonia, by cyclocondensation with glyoxylic acid hydrate (GAH) in diethyl ether at room temperature. The primary *o*-phosphanylanilines prefer reaction with two equivalents of GAH. Cocondensation with *p*-toluidine in a 1:2:2 M ratio furnished a defined product with benzazaphospholine-2-carboxylic skeleton and N-tolylglycinyl group at phosphorus. A branched alkyl group at phosphorus gives rise to preferred formation of *trans*-diastereoisomers with the P lone-pair and 2-COOH group at the same side. This is suitable for formation of chelate complexes and led in combination with $Ni(COD)_2$ in THF to formation of efficient catalysts for conversion of ethylene to mixtures of liquid oligomers and waxy low molecular weight polymers. Both oligomers and polymers display a strongly preferred linear α-olefin architecture, typical for ethylene conversion by neutral P^O-NiR chelate catalysts. Bulky *N*-substituents at the benzazaphospholine-2-carboxylate ligand are essential for high ethylene conversion and bulky *P*-substituents increase the conversion rate.

4. Experimental

General. All operations were performed under argon atmosphere using freshly distilled ketyl-dried solvents. *N*-Methyl- [9] and *N*-neopentyl-2-phosphanylaniline [1a] were prepared by reduction of the corresponding diethylphosphonoanilines with $LiAlH_4$. Other chemicals were purchased and used without further treatment. NMR spectra were measured on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Chemical shifts (δ) are given in ppm relative to Me_4Si (or characteristic solvent signals calibrated with Me_4Si) and H_3PO_4 (85%), respectively. Coupling constants refer to J_{HH} in ^1H and J_{PC} in ^{13}C NMR data unless stated otherwise. ^1H NMR spectra of polymers were measured at 100 °C, using concentrated solutions of the polyethylene samples prepared by swelling for 1 d at 120 °C under argon in C_6D_5Br (*p*-C*H*, δ = 7.23 as reference). HRMS measurements were performed in the Department Chemie, Ludwigs-Maximilians-Universität München, using a MS700 (Jeol) (DEI) and in the Institut für Organische Chemie, Universität Göttingen, using a micrOTOF spectrometer (ESI in MeOH). Elemental analyses were carried out with CHN analyser MICRO CUBE from Elementar vario under standard conditions. The equipment and general procedure for the ligand screening in the batch oligo- and polymerization of ethylene was as reported earlier.[10] GC analyses of flash-distilled oligomers were carried out using a gas chromatograph Hewlett Packard 5890, column HP-5 (30 m) (crosslinked 5% PhMe silicone), 40–150 °C, 10 min isotherm, 4 °C/min; FID.

4.1. N-Methyl-2-isopropylphosphanylaniline (*1a*)

Sodium (181 mg, 7.87 mmol) was dissolved in ca. 30 mL liquid ammonia at −60 °C. Then, a solution of *N*-methyl-2-phosphanylaniline (1.06 g, 7.62 mmol) in diethyl ether (ca. 10 mL) was added at

the same temperature. Within 10 min the dark blue solution turned via blue-green to yellow. Addition of a solution of isopropylbromide (0.75 mL, 7.99 mmol) in ether (ca. 10 mL) at −50 °C and removal of the cooling led to a colorless suspension after some minutes when NH_3 started to vaporize. After reaching room temperature the precipitate was filtered off, washed twice with ether (10 mL), and the solvent removed in vacuum from the filtrate. NMR monitoring displayed ca. 85 mol% of **1a**, ca. 10 mol% *N*,*P*-diisopropyl-*N*-methyl-2-phosphanylaniline and ca. 5 mol% of another side product ($\delta^{31}P = -18$). Distillation at 10^{-3} mbar/51–53 °C gave 740 mg colorless oil in a first fraction and 250 mg in a second fraction (53–54 °C). NMR spectra indicated only marginal shifts in the composition (85:11:4 and 83:8:9 mol%, respectively). This slightly contaminated **1a** (corrected yield 61%) was used for the synthesis of **2a**. ^{1}H NMR ($CDCl_3$): $\delta = 1.07$ (dd, $^3J_{PH} = 25.7$, $^3J = 7.2$ Hz, 3H, Me_A), 1.12 (dd, $^3J_{PH} = 21.9$, $^3J = 6.8$ Hz, 3H, Me_B), 2.20 (m, 1H, PCH), 2.86 (s, 3H, NMe), 3.82 (dd, $^1J_{PH} = 216.8$, $^3J = 5.7$ Hz, 1H, PH), 4.53 (br s, 1H, NH), 6.59 (br dd, $^3J = 8.3$, $^4J_{PH} = 3.8$ Hz, 1H, H-6), 6.66 (br t, $^3J = 7.5$, 6.8 Hz, 1H, H-4), 7.26 (ddd, $^3J = 8.3$, 7.3, $^4J = 1.5$ Hz, 1H, H-5), 7.36 (td, $^3J = 7.2$, $^4J = 1.5$ Hz, 1H, H-3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.99$ (d, $^2J = 18.6$ Hz, Me_A), 22.94 (d, $^2J = 10.6$ Hz, Me_B), 23.82 (d, $^1J = 5.3$ Hz, PCH), 31.17 (s, NMe), 110.55 (br s, CH-6), 117.86 (d, $^1J = 5.3$ Hz, C_q-2), 117.91 (partly superimposed d, $^3J = 4.0$ Hz, CH-4), 131.86 (CH-5), 138.54 (d, $^2J = 8.0$ Hz, CH-3), 153.31 (d, $^2J = 13.3$ Hz, C_q-1); for data in C_6D_6 see Fig. S1. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -47.7$ ppm. HRMS (DEI): $C_{10}H_{16}NP$ (181.22), calcd. for $[M]^+$ 181.1020; found: 181.1011.

4.2. N-Neopentyl-2-neopentylphosphanylaniline (*1b*)

A solution of *N*-neopentyl-2-phosphanylaniline (1.94 g, 9.94 mmol) in diethyl ether (ca. 10 mL) was added at −60 °C to a solution of sodium (251 mg, 10.9 mmol) in ca. 50 mL liquid ammonia. After the color had turned from dark blue to yellow, a solution of neopentylbromide (1.37 mL, 10.9 mmol) in ether (ca. 10 mL) was added at −55 °C. The reaction started only during evaporation of NH_3 and was slow. A colorless solution and precipitate was formed after ca. 3 h at room temperature. The precipitate was then filtered off and washed twice with ether (10 mL). The solvent was removed in a vacuum. NMR monitoring of the crude product (2.49 g) displayed 86 mol% of **1b** (corrected yield 81%) along with 14 mol% unconverted *N*-neopentyl-2-phosphinoaniline, which was removed by vacuum distillation into a Schlenk cooling trap. The residue was then distilled at 10^{-2} mbar/90 °C (bath) to give a viscous colorless oil (95% **1b**). ^{1}H NMR ($CDCl_3$): $\delta = 0.93$ (s, 9H, $NCCMe_3$), 1.08 (dd, $^4J_{PH} = 0.8$ Hz, 9H, $PCCMe_3$), 1.63 (ddd, $^2J = 13.6$, $^3J = 9.2$, $^2J_{PH} = 2.1$ Hz, 1H, PCH_A), 2.12 (ddd, $^2J = 13.6$, $^3J = 6.8$, $^2J_{PH} = 6.0$ Hz, 1H, PCH_B), 2.80 (dd, $^2J = 11.7$, $^3J = 6.4$ Hz, 1H, NCH_A), 2.86 (dd, $^2J = 11.7$, $^3J = 6.4$ Hz, 1H, NCH_B), 3.99 (ddd, $^1J_{PH} = 214.6$, $^3J = 9.2$, 7.2 Hz, 1H, PH), 4.77 (vbr q, $^3J = 5.7$ Hz, 1H, NH), 6.64 (br dd, $^3J = 8.3$, $^4J_{PH} = 3.8$ Hz, 1H, H-6), 6.81 (br t, $^3J = 7.5$, 7.2 Hz, 1H, H-4), 7.31 (ddd, $^3J = 8.3$, 7.2, $^4J = 1.5$ Hz, 1H, H-5), 7.56 (td, $^3J = 7.2$, $^4J = 1.5$ Hz, 1H, H-3). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 28.40$ (s, CMe_3), 31.11 (d, $^3J = 9.3$ Hz, CMe_3), 31.72 (d, $^2J = 10.6$ Hz, CMe_3), 32.41 (s, CMe_3), 38.10 (d, $^1J = 10.6$ Hz, NCH_2), 56.56 (s, NCH_2), 111.14 (d, $^3J = 2.7$ Hz, CH-6), 118.90 (d, $^1J = 6.6$ Hz, C_q-2), 118.04 (d, $^3J = 5.3$ Hz, CH-4), 131.60 (CH-5), 137.79 (d, $^2J = 8.0$ Hz, CH-3), 152.45 (d, $^2J = 13.3$ Hz, C_q-1). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -86.8$ ppm. HRMS (ESI): $C_{16}H_{28}NP$ (265.37), calcd. for $[M+H]^+$ 266.2032; found: 266.2042.

4.3. 1-Methyl-3-isopropyl-2,3-dihydro-1,3-benzazaphosphole-2-carboxylic acid (*2a*)

A sample of the first fraction (219 mg, ca. 1.21 mmol **2a**), dissolved in diethyl ether (5 mL) was added at room temperature into a solution of glyoxylic acid hydrate (111 mg, 1.205 mmol) in the same solvent (20 mL). After stirring overnight the precipitate was filtered off, washed with ether and the solvent removed from the filtrate to give 260 mg crude oily product, which solidified after some time. NMR monitoring showed a strong signal for the *trans*-diastereoisomer of **2a**, a weak signal for *cis*-**2a** (*trans:cis* ca. 90:10% by ^{1}H NMR integration), trace signals of acyclic PCH(OH)-COOH species and trace signals of a PH and P-oxide impurity ($\delta^{31}P = 1.85, -6.69, 0.89, 5.16, -37.51, 51.52$ ppm; relative intensities: 74:9:6:4:4:3 int.%), corresponding to ca. 75% yield of *trans*/*cis*-**2a**. The compound is sensitive to air oxidation and also to reactive sites in silica gel. Slow column chromatography led to extensive decomposition but rapid column chromatography (within ca. 15 min) of an aliquot on silica gel using hexane/30% ethyl acetate furnished ca. 50 mg pure *trans*-**2a**. ^{1}H NMR ([D_8]THF): $\delta = 0.93$ (dd, $^3J_{PH} = 14.2$, $^3J = 7.0$ Hz, 3H, Me_A), 1.07 (dd, $^3J_{PH} = 15.1$, $^3J = 6.8$ Hz, 3H, Me_B), 1.69 (sept d, $^3J = 7$, $^3J_{PH} = 2.8$ Hz, 1H, PCH), 2.91 (s, 3H, NMe), 4.33 (d, $^2J_{PH} = 2.3$ Hz, 1H, $PCH_{trans\ to\ lp}$), 6.41 (br d, $^3J = 8.0$ Hz, 1H, H-7), 6.57 (tdd, $^3J = 7.2$, $^4J_{PH} = 2.3$, $^4J = 0.8$ Hz, 1H, H-5), 7.14 (br td, $^3J = 8.0$, $^4J \approx 1.5$ Hz, 1H, H-6), 7.22 (ddd, $^3J = 6.8$, $^3J_{PH} = 5.3$, $^4J \approx 1.2$ Hz, 1H, H-4), 10.3 (vbr s, 1H, COOH). $^{13}C\{^1H\}$ NMR ([D_8]THF): $\delta = 18.18$ (d, $^2J = 15.9$ Hz, Me_A), 18.92 (d, $^2J = 18.8$ Hz, Me_B), 27.73 (d, $^1J = 18.6$ Hz, PCH), 34.27 (s, NMe), 67.06 (d, $^1J = 23.9$ Hz, PCHN), 107.34 (CH-7), 116.94 (d, $^4J = 8.0$ Hz, CH-6), 123.26 (d, $^1J = 11.9$ Hz, C_q-3a), 131.08 (CH-5), 131.56 (d, $^2J = 22.6$ Hz, 4-CH), 155.32 (C_q-7a), 172.98 (d, $^2J = 13.3$ Hz, COOH); for data in CD_3OD see Fig. S3. $^{31}P\{^1H\}$ NMR: $\delta = 1.8$ ([D_8]THF), 4.7 (CD_3OD) ppm. HRMS (DEI): $C_{12}H_{16}NO_2P$ (237.23), calcd. for $[M]^+$ 237.0919; found: 237.0907. Characteristic signals of *cis*-**2a**: ^{1}H NMR ([D_8]THF): $\delta = 0.81$ (dd, $^3J_{PH} = 11.0$, $^3J = 7.2$ Hz, Me_A; Me_B and CH superimposed), 2.81 (s, NMe), 4.32 (d, $^2J_{PH} = 9.8$ Hz, $PCH_{cis\ to\ lp}$), aryl-H superimposed; characteristic PCH signals of PCH(OH)COOH species in the crude product: ^{1}H NMR ($CDCl_3$): $\delta = 4.56$ (d, $^2J_{PH} = 5.3$ Hz, $PCH_{trans\ to\ lp}$), 4.72 d, $^2J_{PH} = 8.7$ Hz, $PCH_{cis\ to\ lp}$); $^{31}P\{^1H\}$ NMR: $\delta = -6.7$ ([D_8]THF), −4.3 (CD_3OD) ppm.

4.4. 1-Neopentyl-3-neopentyl-2,3-dihydro-1,3-benzazaphosphole-2-carboxylic acid (*2b*)

An ethereal solution (5 mL) of **1b** (120 mg, ca. 0.45 mmol) was added at room temperature into a solution of glyoxylic acid hydrate (42 mg, 0.46 mmol) in the same solvent (20 mL). After stirring overnight the precipitate was filtered off using Celite and washed with ether. Removal of the solvent gave 125 mg (85 %) oily crude product. Rapid column chromatography on silica gel using hexane/ethyl acetate (2 %) furnished a viscous oil. NMR monitoring showed the signals for **2b**, *trans*/*cis*-ratio in the major fraction ca. 58:42% (by ^{1}H NMR integration), in a small second fraction ca. 80:20%. *trans*-**2b**: ^{1}H NMR (CD_3OD): $\delta = 1.01$ (s, 9H, $NCCMe_3$), 1.08 (br s, 9H, $PCCMe_3$), 1.32 (br d, $^2J = 14.4$ Hz, 1H, PCH_A), 2.02 (br dd, $^2J = 14.4$, $^2J_{PH} = 4.3$ Hz, 1H, PCH_B), 2.66 (br d, $^2J = 15.1$ Hz, 1H, NCH_A), 3.45 (br d, $^2J = 15.1$ Hz, 1H, NCH_B), 4.49 (d, $^2J_{PH} = 2.6$ Hz, 1H, $PCH_{trans\ to\ lp}$), 6.59 (superimposed br d, $^3J = 8.3$ Hz, 1H, H-7), 6.63 (tdd, $^3J = 8.3$, 7.2, $^4J_{PH} = 2.6$, $^4J = 0.8$ Hz, 1H, H-5), 7.16 (br td, $^3J = 8.3$, 7.2, $^4J \approx 1.1$ Hz, 1H, H-6), 7.27 (ddd, $^3J = 7.2$, $^3J_{PH} = 6.4$, $^4J \approx 1.1$ Hz, 1H, H-4); COOH probably below solvent-OH). $^{13}C\{^1H\}$ NMR (CD_3OD): $\delta = 28.76$ (s, CMe_3), 31.31 (d, $^3J = 8.0$ Hz, CMe_3), 32.31 (d, $^2J = 11.9$ Hz, CMe_3), 35.99 (s, CMe_3), 46.80 (d, $^1J = 23.9$ Hz, PCH_2), 60.50 (s, NCH_2), 71.37 (d, $^1J = 19.9$ Hz, PCHN), 109.17 (CH-7), 118.14 (d, $^4J = 9.3$ Hz, CH-6), 125.38 (d, $^1J = 8.6$ Hz, C_q-3a), 131.16 (CH-5), 131.68 (d, $^2J = 25.2$ Hz, 4-CH), 155.97 (C_q-7a), 176.14 (d, $^2J = 14.6$ Hz, COOH). $^{31}P\{^1H\}$ NMR (CD_3OD): $\delta = -17.3$ ppm. ***cis*-2b**: ^{1}H NMR (CD_3OD): $\delta = 0.97$ (s, 9H, $NCCMe_3$), 1.06 (br s, 9H, $PCCMe_3$), 1.46, 1.47 (2 dd, $^2J = 14.7$, $^2J_{PH} = 5.1$ Hz, 1H, PCH_A), 1.85 (br dd, $^2J = 14.7$, $^2J_{PH} = 4.3$ Hz, 1H, PCH_B), 2.79 (br d,

^2J = 15.5 Hz, 1H, NCH_A), 3.40 (br d, ^2J = 15.5 Hz, 1H, NCH_B), 4.79 (d, $^2J_{PH}$ = 17.0 Hz, $PCH_{cis\ to\ lp}$), 6.49 (br d, ^3J = 8.3 Hz, 1H, H-7), 6.60 (superimposed tdd, 1H, H-5), 7.05 (br td, ^3J = 8.3, 7.3, $^4J \approx$ 1.5 Hz, 1H, H-6), 7.11 (superimposed br t, 1H, H-4); COOH probably below solvent-OH). $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 29.08, 29.12 (2s, CMe_3), 31.27 (d, ^3J = 9.3 Hz, CMe_3), ca. 31.3 (superimposed d, CMe_3), 35.45 (s, CMe_3), 45.31 (d, ^1J = 29.2 Hz, PCH_2), 59.67 (s, NCH_2), 68.66 (d, ^1J = 26.5 Hz, PCHN), 108.74 (CH-7), 118.47 (d, ^4J = 6.6 Hz, CH-6), 125.83 (d, ^1J = 8.0 Hz, C_q-3a), 129.86 (d, ^2J = 18.6 Hz, 4-CH), 130.21 (CH-5), 154.96 (d, ^2J = 4.0 Hz, C_q-7a), 172.81 (s, COOH). $^{31}P\{^1H\}$ NMR (CD_3OD): δ = −17.9, −18.1 ppm. (The occurrence of two close, similar intense signals for P, PCH_A and CMe_3 of the *N*-Np group hints at hindered rotation in the *cis*-diastereoisomers and slightly different signals of these nuclei if the neopentyl groups are directed to the same or opposite sides of the ring.) HRMS of *trans*/*cis*-**2b** (ESI): $C_{18}H_{28}NO_2P$ (321.39), calcd. for $[M+H]^+$ 322.1930; found: 322.1931.

4.5. 1-Neopentyl-3-(N-p-tolyl)glycinyl-2,3-dihydro-1, 3-benzazaphosphole-2-carboxylic acid (**3**)

A solution of glyoxylic acid hydrate (500 mg, 5.43 mmol) in diethyl ether (10 mL) was added slowly to a solution of *N*-neopentyl-2-phosphanylaniline (53 mg, 2.73 mmol) and *p*-toluidine (580 mg, 5.41 mmol) in diethyl ether (25 mL). After stirring for 24 h (to complete the conversion) the white precipitate was collected, washed with small amounts of ether and dried in vacuum to yield 0.77 g (68%) white powder. ^1H NMR ([D$_8$]THF, Ref. THF): δ = 0.84 (s, CMe_{3A}) and 0.94 (s, CMe_{3B}; A:B = 42:56%), 1.97 (s, *p*-Me_B), 2.03, 2.04, 2.05 (3s superimposed), 2.24 (s, *p*-Me_A), 2.62 (d, $^2J \approx$ 16 Hz, H_{Aa}), 2.67 (d, $^2J \approx$ 15 Hz, H_{Ba}), 3.24–3.31 (m, CH_2), 3.32 (d, $^2J \approx$ 16 Hz, H_{Ab}), 3.39 (d, ^2J = 15.1 Hz, H_{Bb}), 4.25 (sh) and 4.27 (br s, PCH), 4.73 (d, $^2J_{PC}$ = 2.7 Hz, PCH_A), 4.98 (d, $^2J_{PC}$ = 3.0 Hz, PCH_B), 5.06, 5.10 (br, sbr, NH and/or OH), 6.04 (m, 2 *o*-CH), 6.30–6.77 (m, *o*- und *m*-CH), 7.00–7.23 (m, 4H, aryl), 7.78 (s, 1 H_A, OH oder NH_{Amid}). $^{13}C\{^1H\}$ NMR and DEPT-135 ([D$_8$]THF, ref. THF): δ = 20.20 (s, *p*-Me_A), 20.31 (s, *p*-Me_B), 28.35 (s, CMe_{3A}), 28.42 (s, CMe_{3B}), 35.06 (s, CMe_3), 57.33 (br d, ^1J = 25.4 Hz, PCH_B), 57.39 (br d, ^1J = 25.2 Hz, PCH_A), 60.46 (s, NCH_{2A}), 60.53 (s, NCH_{2B}), 68.44 (d, ^1J = 23.0 Hz, PCH_{Aring}), 68.52 (d, ^1J = 23.9 Hz, PCH_{Bring}), 108.60 (s, 7-CH_B), 108.95 (s, 7-CH_A), 114.34 (2 superimposed s, *o*-CH), 114.89 (s, *o*-$CH_{B\ or\ A}$), 117.29 (d, ^3J = 8.7 Hz, 5-CH), 117.59 (d, ^3J = 8.3 Hz, 5-CH), 120.10 (d, ^1J = 13.7 Hz, 3-C_{qA}), 120.40 (d, ^1J = 12.0 Hz, 3-C_{qB}), 122.15 (s, *o*-CH_A), 125.65 (s, *p*-C_{qA}), 127.04, 127.07 (2s, *p*-C_{qB}), 129.54 (s, *m*-$CH_{B\ or\ A}$), 129.76, 129.80 (2s, *m*-CH_B), 130.37 (s, *m*-CH_A), 131.49 (s, 6-CH_B), 131.54 (s, 6-CH_A), 132.69 (d, ^2J = 24.2 Hz, 4-CH), 133.32 (d, ^2J = 23.9 Hz, 4-CH), 146.36 (d, $^3J \approx$ 7.3 Hz, *i*'-C_{qA}), 146.53 (d, $^3J \approx$ 7 Hz, *i*'-C_{qB}), 151.35 (s, 7a-C_{qA}), 156.86 (s, 7a-C_{qB}), 172.28 (d, ^2J = 12.0 Hz, $COOH_A$), 172.50 (d, ^2J = 13.3 Hz, $COOH_A$), 172.72 (d, ^2J = 12.0 Hz, $COOH_B$). $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = −4.54 ppm (A), −6.10 ppm (B), signal intensity ratio A:B = 4:5 (43:57%). In solution slow decomposition occurs, indicated by small signals at −21.9, −24.2, −24.9, −41.7 and −129.0 ppm after a long measuring time for ^{13}C nuclei. Analysis calcd. for $C_{29}H_{36}N_3O_4P$ (521.59): C 66.78, H 6.96, N 8.06; found: C 66.48, H 6.43, N 7.65.

4.6. Ethylene oligomerization/polymerization

2a and **2b**, respectively, and $Ni(COD)_2$ (quantities see Table 2) were dissolved in THF. Then the ligand solution was added to the pale yellow $Ni(COD)_2$ solution and the resulting intense yellow solution transferred into the autoclave. After pressurizing, determination of weight difference and tightness check the autoclave was heated to 70, 80, 90 °C (each ca. 30 min) and finally to 100 °C, required for the start of the conversion (in exp. 4 start and slow reaction already at 90 °C). The reaction was allowed to run overnight (ca. 15 h) with pressure registration. After cooling to ca. 20 °C unconverted ethylene was released. Butenes and small amounts of hexenes and THF were condensed in a cooling trap (−20 °C). The remaining product was transferred to a flask, and volatiles were flash distilled (80–100 °C/1 Torr) into a cooling trap (−196 °C). Residual polymer waxes were stirred for 1 d with methanol/hydrochloric acid (1:1), washed with methanol and dried in vacuum. Conversion, characteristic data of polymers and composition of flash distilled oligomers are given in Table 2.

4.7. Crystal structure analysis of **2a**

Crystal data: Triclinic, space group $P\bar{1}$, a = 5.2089(4), b = 8.8838(4), c = 13.5003(7) Å, α = 84.168(4), β = 89.312(5), γ = 81.657(5)°, V = 614.91(6) Å^3, Z = 2, D_x = 1.281 Mg/m^3, μ = 1.870 mm^{-1}, $F(000)$ = 252. A colourless tablet 0.20 × 0.15 × 0.08 mm was mounted on a glass fibre in inert oil. A total of 25388 data (2547 unique, R_{int} 0.037) were recorded at 100 K on an Oxford Diffraction Nova E diffractometer using mirror-focussed Cu Kα radiation (λ = 1.54184 Å) in the range θ = 3.3–75.7° (99.8% completeness to θ = 75°). Absorption corrections were semi-empirical from equivalents. The structure was refined by full-matrix least-squares on F^2 [11]. The OH hydrogen was refined freely; other hydrogen atoms were included using a riding model or rigid methyl groups. The final *wR*2 was 0.077 for 401 parameters and all reflections, with *R*1 ($I > 2\sigma(I)$) 0.029; *S* 1.05, max. $\Delta\rho$0.58 e Å^{-3}. Complete crystallographic data for **2a** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 976535. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged (HE1997/14-1). Dr. habil. D.G.Yakhvarov and O.S.Fomina thank the Russian Foundation for Basic Research (RFBR) and Tatarstan Academy of Sciences (research project No. 12-03-97067-r_povolje_a) for support of this research activity. We thank Dr. M. K. Kindermann, G. Thede and M. Steinich for numerous NMR spectra, Prof. Dr. H.-C. Böttcher and B. Breitenstein (Department Chemie, Ludwig-Maximilians-Universität München) for HRMS (DEI) and Dr. H. Frauendorf and G. Sommer-Udvarnoki (Georg-August-Universität Göttingen, Institut für Organische und Biomolekulare Chemie) for HRMS (ESI) measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.03.046.

References

[1] (a) B.R. Aluri, M.K. Kindermann, P.G. Jones, J.W. Heinicke, Chem. Eur. J. 14 (2008) 4328;
(b) M. Ghalib, P.G. Jones, S. Lysenko, J.W. Heinicke, Organometallics 33 (2014) 804.
[2] K. Issleib, G. Thomas, Chem. Ber. 93 (1960) 803.
[3] (a) W. Keim, Angew. Chem., Int. Ed. Engl. 29 (1990) 235;
(b) D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous Phase Organometallic Catalysis: Concepts and Applications, Wiley-VCH, Weinheim, 1998, p. 541;
(c) J. Heinicke, N. Peulecke, M. Köhler, M. He, W. Keim, J. Organomet. Chem. 690 (2005) 2449;
(d) P. Braunstein, Chem. Rev. 106 (2006) 134;
(e) P. Kuhn, D. Sémeril, D. Matt, M.J. Chetcuti, P. Lutz, Dalton Trans. (2007) 515.
[4] (a) J. Heinicke, N. Peulecke, P.G. Jones, Chem. Commun. (2005) 262;
(b) J. Lach, C.-Y. Guo, M.K. Kindermann, P.G. Jones, J. Heinicke, Eur. J. Org. Chem. (2010) 1176;

(c) J. Heinicke, J. Lach, K.R. Basvani, N. Peulecke, P.G. Jones, M. Köckerling, Phosphorus Sulfur Silicon Rel. Elem. 186 (2011) 666;
(d) O.S. Fomina, D.G. Yakhvarov, J. Heinicke, O.G. Sinyashin, Uchenye Zapiski Kazanskogo Universiteta 154 (2012) C13.
[5] (a) J. Heinicke, K.R. Basvani, P.G. Jones, Phosphorus Sulfur Silicon Rel. Elem. 186 (2011) 678;
(b) R. Basvani, PhD thesis, Ernst-Moritz-Arndt-University Greifswald 2012.
[6] (a) K. Issleib, H. Oehme, Chem. Ber. 100 (1968) 2685;
(b) K. Issleib, H. Oehme, R. Kümmel, E. Leißring, Chem. Ber. 101 (1968) 3619;
(c) K. Issleib, H.-U. Brünner, H. Oehme, Organometal. Chem. Synth. 161 (1970/1971) 161.
[7] (a) N. Peulecke, M.K. Kindermann, M. Köckerling, J. Heinicke, Polyhedron 41 (2012) 61;
(b) K.R. Basvani, O.S. Fomina, D.G. Yakhvarov, J. Heinicke, Polyhedron 67 (2014) 306.
[8] L.D. Quin, J.J. Breen, Org. Magn. Reson. 5 (1973) 17.
[9] M. Ghalib, B. Niaz, P.G. Jones, J.W. Heinicke, Heteroatom Chem. 24 (2013) 452.
[10] J. Heinicke, M. Köhler, N. Peulecke, M. He, M.K. Kindermann, W. Keim, G. Fink, Chem. Eur. J. 9 (2003) 6093.
[11] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.