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α-Phosphanyl amino acids: synthesis, structure and properties of alkyl and heterocyclic *N*-substituted diphenylphosphanylglycines

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Dedicated to Professor Dr. Dr. h.c. Manfred Scheer on the occasion of his 60th birthday

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ABSTRACT

N-Alkyl and *N*-heterocyclic substituted diphenylphosphanylglycines **1a**–**j** were synthesized by a convenient one-pot, three-component reaction of diphenylphosphane, the corresponding primary amine and glyoxylic acid hydrate in diethyl ether. Phosphanylglycolates **2** and phosphoniobis(glycolates) **3** were detected as intermediates. In the case of steric hindrance or low basicity of the amine only **2** or mixtures of **2** and **1** are formed. Reactivity studies of selected phosphanylglycines showed facile decarboxylation and hydrolysis, oxidation and formation of coordination compounds with BH_3 or $W(CO)_5$. *N*-Alkyl derivatives (*tert*-butyl, *n*-hexyl, benzhydryl) with moderate steric hindrance reacted with Ni(COD)$_2$ in THF or toluene in the presence of ethylene with heating under pressure to yield highly active oligomerization catalysts, and converting the ethylene to liquid and low-molecular-weight solid ethylene oligomers (M_{NMR} 500–1250 g/mol) with high selectivity for linear α-olefins. Smaller *N*-alkyl or *N*-heterocyclic amino substituents at the phosphanyl acetic skeleton interfere with the ethylene conversion and deactivate the catalyst. The structures of the compounds were elucidated by solution NMR and single crystal XRD studies.

1. Introduction

Synthetic amino acids have found interest and applications in many fields of chemistry, biochemistry and pharmacy.[1] Introduction of a phosphanyl group into amino acids and peptides, useful particularly as coordination site for transition metals in low oxidation states, was accomplished by various strategies.[1b,2–11] Many products were utilized for a variety of transition metal catalyzed[2,3] or organocatalyzed[4] chemical transformations. Another goal was the use of water soluble phosphane derivatives as carriers for pharmaceutically interesting transition metals.[5] The known types of phosphanyl amino acids involve *a*) directly *N*-phosphanylated compounds, formed by reaction of the amino acids with $ClPPh_2$,[6] *b*) acyclic and heterocyclic *N*-phosphanylmethyl derivatives, prepared by condensation reactions of *N*–CH_2OMe substituted amino acids with secondary phosphanes[7] or of free amino acids, their salts and esters with formaldehyde and phosphanes or their addition products R_2PCH_2OH and $RP(CH_2OH)_2$,[2,8,9] and *c*) amino acids with the phosphanyl function at the α-C side group. The latter were obtained by Pd-catalyzed coupling of secondary phosphanes with *O*-triflate or *O*-mesylate derivatives of serine, proline or tyrosine[3] or alternatively by reaction of phosphides with the halogenated amino acids under appropriate conditions.[10] α-Phosphonio-*N*-acyl amino acid derivatives were reported by Mazurkiewicz et al.[1b] and the first *N*-tert-butyl and *N*-aryl derivatives of glycine with a phosphanyl substituent directly bound at the α-C atom were synthesized by us in a convenient one-pot three-component reaction.[11] Principally, the structural features of these compounds offer the potential for formation of five-membered P,COO^- or N,COO^- chelate complexes, to act as tripod P,N,COO^- ligand or as soft-hard hybrid ligand for bimetallic complexes. This prompted us to explore the scope and limits of the three-component synthesis for a wider variety of *N*-substituents and to illuminate general properties and some aspects of their reactivity. Because of the close structural relationship to diphenylphosphanylacetic acid,[12] applied as phosphanylcarboxylate nickel catalyst in the industrial ethylene oligomerization within the SHOP

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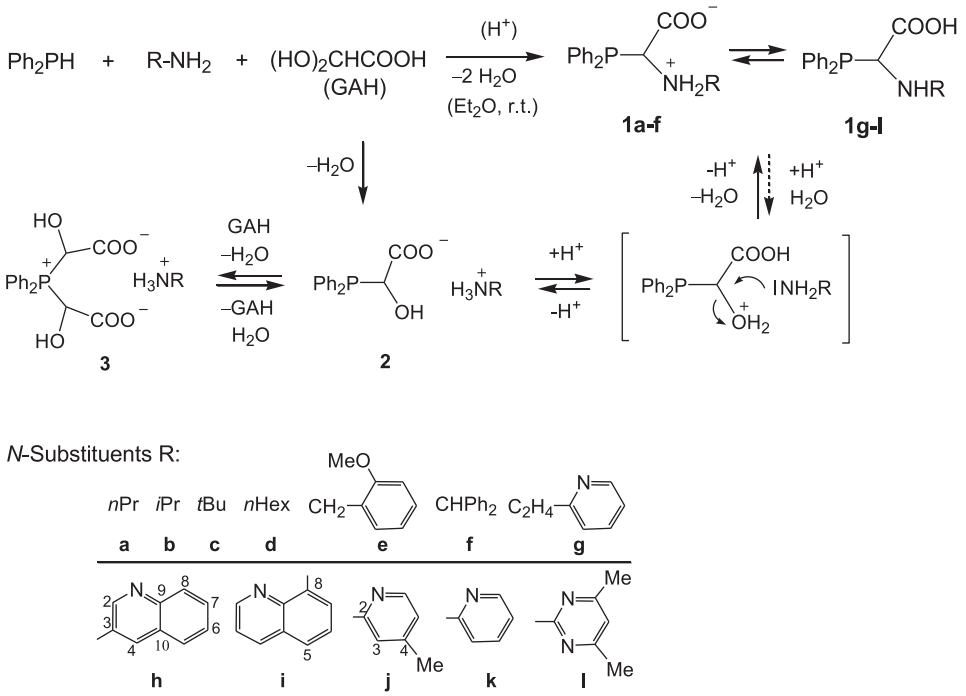
process,[13,14] ligand screening for in situ formation of nickel catalysts for ethylene oligomerization was also undertaken in this study.

2. Results and discussion

2.1. Synthesis

Three-component aminomethylations of trivalent PH-compounds with primary or secondary amines and formaldehyde are well known,[15] but knowledge about analogous reactions with other aldehydes is still sparse and restricted to arylaldehydes in THF.[16] The resulting α-phosphanyl benzylamines, preferably prepared till now by addition of R_2PH or R_2PM^I (M=Na or Li) at benzaldimines or their hydrochlorides, are rather unstable in solution but are stabilized by electron-withdrawing *p*-nitrophenyl substituents at the α-C or N atom.[17] The electron withdrawing effect of COOH suggested that phosphanylmethylamines with a COOH group at α-C also are stabilized. This inspired us to develop a convenient synthesis of aminodiphenylphosphanyl acetic acids, in the following named (diphenyl) phosphanylglycines, by three-component one-pot condensations of glyoxylic acid hydrate (GAH) with diphenylphosphane and primary amines. In addition to the recently communicated condensations with $tBuNH_2$ and some primary aryl amines,[11] a variety of linear and branched alkyl-, arylalkyl- and heterocyclic primary amines were used and found applicable in this reaction to give the corresponding phosphanyl glycines **1a**–**j**. However, **1k** and **1l** were formed only in minor amounts in addition to the corresponding phosphanylglycolates **2k** and **2l** (Scheme 1). Nitrogen atoms of *N*-heterocyclic substituents did not interfere with the reaction as long as they did not lower the reactivity of the primary amino group too strong, such as in the case of, e.g. pyrimidin-2-yl amines.

equilibrium concentrations of sparsely soluble products in solution remain low. NMR monitoring of the reaction with *tert*-butylamine revealed that the precipitate, separated after 10 min, contained considerable amounts of the *tert*-butylammonium phosphanylglycolate **2c**, whereas a sample taken from the suspension after stirring for 15 h displayed mainly the phosphanylglycine **1c**. This shows that the three-component synthesis of phosphanylglycines does not proceed via a Mannich reaction with halfaminale and immonium intermediates, as in the case of phosphanylmethylations of amines with formaldehyde,[15a] but that the OH groups of GAH are stepwise protonated and replaced with cleavage of water by the phosphane and subsequently by the amine. The second step is slower so that usually reaction times of 15–24 h were chosen, in the case of slow reactions even several days. The main reason is the presence of the COOH group that lowers the concentration of free amine, but also steric effects or low basicity of the amine diminish the reaction rate. If an excess of amine is used, as tested for with iPr_2NH (1.6 equiv), a mixture of the hydrated phosphanylglycine and its salt (**1b**·0.6$iPrNH_2$·H_2O) precipitated. If 2 equiv of glyoxylic acid were used in the three-component reaction, recently demonstrated with $tBuNH_2$ as amine component, organoammonium phosphanylbis(glycolates) **3** are formed in high yield.[11c,d] The analogous diethyl ammonium salt of **3** was formed also with diethyl amine as the NH component in good yield,[18] in this case, however, even with only 1 equiv of glyoxylic acid. This shows that phosphanylbis(glycolates) **3** may also be involved in the equilibrium reactions leading to the phosphanylglycines (Scheme 1). Disubstitution at the primary amino group, typical for many phosphanylmethylations, was never observed. The mono-phosphanylmethylations, known also for *N*-primary α-amino acids such as alanine under mild conditions,[19] may thus be attributed to the presence of the COOH group in α-position.



Scheme 1. Three-component synthesis of *N*-substituted diphenylphosphanylglycines **1a**–**l** via organoammonium diphenylphosphanylglycolates **2**, unless the latter are stabilized by bulky or electron-withdrawing substituents R.

The conversions were performed in a 1:1:1 reactant ratio at room temperature (20–24 °C), best in diethyl ether by addition of the ethereal solution of the phosphane and amine to an ethereal solution of glyoxylic acid hydrate (GAH) or reversed addition. The majority of the products precipitate in this solvent. This not only facilitates the isolation but also increases the yield, as the

The water, liberated in the condensation into the crude reaction mixtures, results in still minor equilibrium amounts of **2**. Attempts to remove this water from the suspensions by neutral drying agents $CaCl_2$ or $MgSO_4$, introduced into the reaction encapsulated in an immersed fritted glass, did not result in significant conversion of the minor residual amount of **2c** to **1c**. Alternative efforts to remove

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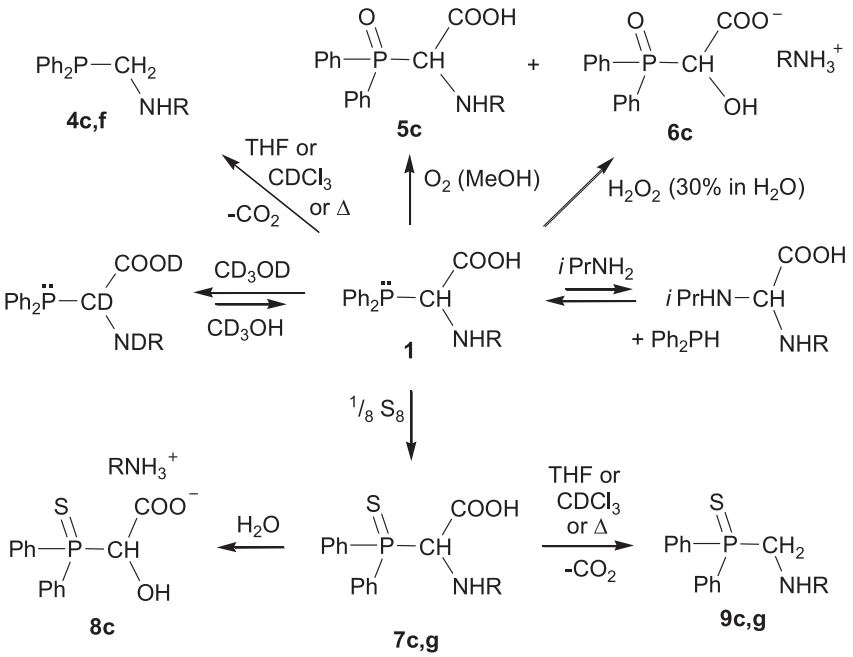
the reaction water by distillation of wet diethyl ether, methanol or benzene resulted in decomposition. Thus, distillation of wet methanol from a solution of crude **1c** led to the decarboxylation product Ph_2PCH_2NHtBu (**4c**) and its salts with the anions of **2** ($\delta^{31}P=-20.0/6.8$) and of *meso*/*rac*-**3** ($\delta^{31}P=-19.4/26.1$, 27.1). Purification of the separated crude phosphanylglycines succeeded, however, by crystallization from dry methanol at room temperature. The crude products, in some cases monohydrates, have very good solubility in this solvent while the majority of the methanol solvates of **1** precipitate or crystallize from the MeOH solution with somewhat lower solubility. Some products lost methanol on drying under vacuum, but *N*-alkyl or *N*-arylalkyl phosphanylglycine methanol solvates were usually stable under vacuum at room temperature.

2.1.1. Limitations. Whereas no limitations were observed for the first step in the three-component condensations, the slower replacement of the second OH group by an amino group can be strongly hindered, e.g. in the case of sterically demanding substituted primary amines. Thus, in the case of 1-adamantylamine the adamantylammonium phosphanylglycolate only converted slowly and partly (after 3 d 10%) to the respective *N*-adamantyl phosphanylglycine. In methanol, this conversion was faster but also limited to 40% after 3 d.[11d] In the case of secondary amines such as diethylamine[18a] or *N*-methylaniline,[11b] the second condensation step does not take place. Heating for thermal condensation and removal of reaction water from the equilibrium is not possible because of the generally easy decarboxylation of phosphanylglycines.

Besides steric effects, electronic effects, *i.e.* low basicity of the primary amine, also slow down or prevent the conversion of organoammonium phosphanylglycolates to phosphanylglycines. Thus, the reactions of 2-aminopyridine and of 2-amino-4,6-dimethylpyrimidine with diphenylphosphane and GAH in diethyl ether provided only **2k** and **2l** within 15 h, which in [D_8]THF solution displayed slow partial conversion to **1k** and **1l** (after ca. 10 h at 22–25 °C **2k**:**1k**≈45:55 and **2l**:**1l**≈80:20). Slightly higher basicity, induced by the methyl group in 3-methyl-pyridylamine or by benzene-annulation in the quinolylamines, was sufficient to enable formation of the corresponding phosphanylglycines **1h**–**j**. This shows that the slow conversion is not caused by the presence of a competing Lewis-basic nitrogen atom in the heterocyclic substituent but rather by the lowered basicity of the amino group, induced by the electron withdrawing effect of the *N*-substituent. Finally, it should be mentioned that attempts to synthesize *N*-methyl- or *N*-unsubstituted diphenylphosphanylglycines by three-component reaction with $MeNH_2$, NH_3, $(Me_3Si)_2NH$ or $(NH_4)_2CO_3$ as amine component in ethereal solution also failed. It is assumed that lack of any steric hindrance favors other condensations reactions, as known for reactions of glyoxylic acid with ammonia, methyl amine and ethyl amine.[20]

2.2. Properties and reactivity

Phosphanylglycines as well as phosphanylglycolates possess two Lewis-basic substituents at the same carbon and thus behave as P,N and P,O acetales, respectively. The presence of an intrinsic acidic COOH group destabilizes these compounds and causes equilibrium (Scheme 1) and in part decomposition reactions in solution, as illustrated in the following by the solution behavior of **1b** and **1c**. In aqueous and D_2O solution they undergo rapid acid catalyzed replacement of the amino by an OH or OD group, yielding quantitatively the respective organoammonium phosphanylglycolates.[18a] Diluted aqueous bases hydrolyze slower and incomplete, as exemplified by an NMR test of **1c**. A freshly prepared solution of this compound in D_2O, containing 1 equiv of NaOD, displayed strong phosphorus signals of sodium phosphanylglycinate and phosphanylglycolate and small signals of Ph_2PH and Ph_2PD, integral ratio ca. 45:45:4:5. After 10 d at room temperature the ratio was only slightly shifted (ca. 40:50:5:5). Solutions of phosphanylglycines in dry CD_3OD can be stored for several days without significant decomposition in air-tight closed NMR tubes. Only H→D exchange of the acidic α-CH proton occurs (Scheme 2) and in CD_3OD solution leads to the disappearance of the PCHN proton signals and low-intensity ^{13}C multiplets with C–P and C–D coupling, in particular in the case of stronger electron withdrawing *N*-(hetero)aryl substituents.



Scheme 2. Illustration of the reactivity of **1** at room temperature.

Traces of moisture and/or slight excess of amine caused various equilibrium reactions. This was shown for **1b**, which contains ca. one molecule water and 0.6 equiv of excess *i*PrNH; minor signals for temperature dependent equilibrium amounts of Ph_2PD, $Ph_2PCH(OH)COO^-$ RNH_3^+ and $Ph_2P^+(CH(OH)COO^-)_2$ $iPrNH_3^+$ species were observed in the NMR spectra in CD_3OD (see e.g., Supplementary data, Figs. S1 and S2). The sharp doublet of the averaged methyl signals of the *N*-isopropyl group in pure **1b** at room temperature is strongly broadened by these reactions within the NMR time scale and changes to two broad doublets on cooling to −20 °C (Fig. S1), indicating the non-equivalence of the two diastereotopic methyl groups in the asymmetric compound if the processes behind the signal averaging (C–N bond cleavage and formation equilibria) are hindered. The presence of small equilibrium amounts of Ph_2PH, which is rapidly attacked by oxygen, may explain the high sensitivity of the solutions to air oxidation. Involvement of CD_3OD or MeOH in replacing the Ph_2P- or NHR-group in solution equilibria by −OR (R=CD_3 or Me) was not observed.

Phosphanylmethylacetals $Ph_2PCHR'OR$ with R′=H or aryl are known and accessible by acid-catalyzed condensations of Ph_2PH with alcohols and aldehydes,[21] but derivatives with an intrinsic acid substituent R′=COOH are probably instable even in solution and therefore not involved in the equilibrium reactions of phosphanylglycines with nucleophiles. Free equilibrium amounts of $iPrNH_2$, formed from the above mentioned crude **1b**·0.6 $iPrNH_2 \cdot H_2O$ in CD_3OD solution, may partly replace the Ph_2P-group, particularly at elevated temperature (55 °C). Variable temperature (VT) ^{31}P NMR studies of this solution showed a slight increase of the Ph_2PD integrals with the temperature at the expense of the signals of **1b** and **2b**. In [D_8]THF solution this trend is somewhat more pronounced (^{31}P integrals of Ph_2PH; **1b** and **2b** at −20, 25, 40, 55 °C: 3, 9, 13, 20; 89, 82, 78, 69 and 5, 2, 1, 1%) (see Supplementary data, Fig. S2). A lack of H-D exchange in [D_8]THF reveals the PCHN and PCHO proton doublets as well as a new singlet at δ=2.25, like the new *Me*$_2$CH doublets ($\delta \approx 1.20$) it grew in intensity with the temperature. The new singlet has a very similar chemical shift as the methine proton in $(Me_2N)_2CHCOOEt$ (δ=2.33[22]) and may thus be attributed to equilibrium amounts of $(iPr_2N)_2CHCOO^-$ species in solution. Addition of 2.8 equiv of H_2O to this solution increased the content of **2b** at the expense of **1b** while the Ph_2PH content and the effect of increasing temperature was not markedly changed except for a slight preference of **2b** compared to **1b** at higher temperature.

Use of [D_8]THF instead of CD_3OD for solution NMR measurements is advantageous with respect to the appearance of PCHN proton and $^{13}C(H)$ NMR signals but disadvantageous with respect to slow decarboxylation of some phosphanylglycines even at room temperature. In the case of **1c**·MeOH and **1i**·MeOH, partial decarboxylation reached 30–40% within 1 d or prolonged ^{13}C NMR measurements of diluted solutions. Much stronger decarboxylation (≥70%) occurred during attempts to dissolve the phosphanylglycines (*i.e.*, **1c**·MeOH and **1f** to **4c** and **4f**) in $CDCl_3$ with slight warming (Scheme 2). This may be attributed to the lack of stabilizing hydrogen bonds of this solvent. In the solid state the compounds are somewhat more stable. Thus, substantial thermal decarboxylation of solid **1c**·MeOH starts at only 95–100 °C, and the exothermic DTA (5°/min) peak for strong decarboxylation appeared at 114 °C. This behavior is comparable to diphenylphosphanylacetic acid, which undergoes thermal decarboxylation in the same temperature range and decomposes more rapidly in diluted monomer solutions without stabilizing hydrogen bonds to a second molecule or a donor solvent.[23]

Since the reactivity of *P,N*-acetales towards protic solvents or reagents is closely connected with protonation of either N or P, it was initially assumed that blockage of the P-lone pair would increase the stability of the P-substituted glycines. This is the case for many phosphine oxides, -sulfides, -BH_3 or -$W(CO)_5$ complexes compared to the respective phosphanes, where air oxidation also may start by interaction with the P-lone pair.[24] This prompted us to perform some reactivity studies with selected phosphanylglycines. The above mentioned air oxidation of phosphanylglycines in methanol or THF solution led for **1c**·MeOH to a mixture of the phosphinoylglycine **5c** and the phosphinoylglycolate **6c** with ^{31}P resonances at δ=30.6 and 32.0 ppm. Oxidation of **1c**·MeOH with 30% aqueous H_2O_2, due to the sensitivity to hydrolysis, led only to **6c**, which was obtained in pure form also by condensation of Ph_2PHO with GAH.[18a] Oxidation with sulfur is a cleaner reaction and can easily be performed in the absence of water. Reaction of **1c**·MeOH and **1g**·MeOH with sulfur in methanol provided the thiophosphinoylglycines **7c** and **7g**·MeOH in high yields. Various 'sulfur-protected' thiophosphinoyl amino acid derivatives with phosphorus bound at a more remote carbon atom than α-C have found use in the synthesis of phosphanyl peptide transition metal catalysts.[3] This was achieved by performing synthesis and purification of air-stable precursors under aerobic conditions and carrying out selective deprotection of thiophosphinoyl peptides with Raney nickel for the final reaction with transition metal compounds. The thiophosphinoylglycines **7c** and **7g**, however, are similarly sensitive to hydrolysis as *N*-alkyl phosphanylglycines, and this limits their handling under aerobic condition. In the presence of moisture, **8c** is obtained by hydrolysis of **7c**, which was obtained earlier by oxidation of **2c** with sulfur.[18a] Moreover, in [D_8]THF, $CDCl_3$ and even in CD_3OD solution, carbon dioxide is slowly cleaved even at room temperature (for **7g** markedly faster than for **7c**), leading to contaminations by thiophosphinoylmethylamines **9c** and **9g**, respectively.

Protection of the phosphanyl group by a BH_3 substituent, a versatile tool to prevent air oxidation of phosphanes and applicable even in the presence of relatively acidic OH substituents,[25,26] failed in reactions of **1b**–**d**·MeOH with excess $Me_2S \cdot BH_3$ because of the facile reduction of carboxylic acids by BH_3 after primary formation of acyl boron moieties.[27] However, the increased stability of carboxylate salts towards reduction allowed formation of a borane protected *N*-*tert*-butyl-phosphanylglycine derivative by reaction of crude *tert*-butylammonium phosphanylglycolate **2c**[18a] with 2.6 equiv of $Me_2S \cdot BH_3$ in THF at 0 °C. The NMR data are in accordance with the structure proposal **10c** (Scheme 3). Hydrogen evolution indicated reaction of the acidic NH/OH protons with the second equivalent of BH_3, leading to replacement of the glycolate-OH by the *tert*-butylamino group and formation of an acyl borate moiety, indicated by the broad ^{11}B NMR signal at δ=−0.7, close to that of $tBuNH_3^+$ $B(Oac)_4^-$ (δ=−0.5).[28] The P-bound BH_3 did not attack the COO-group. The ^{11}B resonance appeared at δ=−40.5, typically for phosphane-boranes,[29] the ^{13}C carbonyl doublet at δ=169.2, just between the CO resonances of acetic acid anhydride and acetic acid methyl ester (δ=167.4, 171.3) and significantly upfield from the COO resonances of **3c** or free acetic acid and acetates (δ=175–183).[30] The substitution of the OH by the amino group was indicated by the ^{13}C doublet of the α-CH carbon at δ=56.6, the region of the PCHN signals, while the α-CH carbon signal of **2c** is exhibited more downfield at δ=71.1.[18a] The stabilization of **10c**, however, is limited by sensitivity to hydrolysis, like as for the related thiophosphinoyl derivative **7c**. In moist THF it is hydrolyzed with liberation of $Ph_2PH \cdot BH_3$ ($\delta^{31}P$=2.0) and small amounts of Ph_2PH ($\delta^{31}P$=−40.0), in D_2O/CD_3OD it is rapidly decomposed with formation of Ph_2PD.

Finally, we studied the reaction of selected phosphanylglycines, **1c**·MeOH and **1i**·MeOH, with $W(CO)_5(THF)$ in THF to block the phosphorus electron lone pair by coordination of $W(CO)_5$ and to determine the stability and other properties of the (phosphanylglycine)$W(CO)_5$ complexes. The *N*-heteroaryl-substituted complex **11i** was obtained in pure form whereas the *N*-alkyl derivative **11c** proved less stable and was contaminated by $(Ph_2PH)W(CO)_5$

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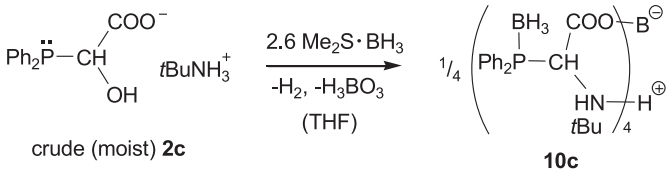
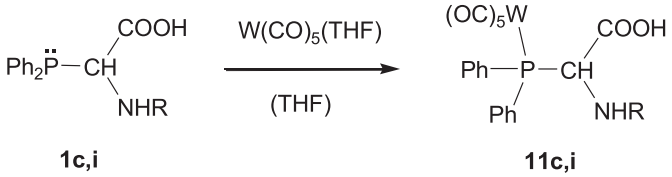


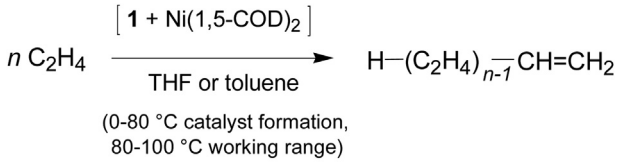
Scheme 3. Formation of a BH_3-protected phosphanylglycine derivative.

(δ^{31}P=−13.7 (satl. d, $^1J_{PW}$=136.6 Hz), lit. δ=−14.8[31]) despite solid **1c**·MeOH was added to the THF solution of $W(CO)_5$(THF) to prevent decomposition of **1c** in solution before complex formation. This technique was found necessary already in our recent investigation on hydrolytically less sensitive *N*-aryl phosphanylglycines (L) to obtain the corresponding $LW(CO)_5$ complexes in pure form.[11b] Attempts at later purification by column chromatography on silica gel led to complete decomposition and formation of a multicomponent mixture, which was not further analyzed. The downfield phosphorus coordination chemical shifts $\Delta\delta_{\mathbf{11-1}}$=23.6 and 27.3 of **11c** in the crude mixture and of **11i** versus **1c** and **1i**, respectively, correspond to values typical for $(Ph_2PR)W(CO)_5$ complexes[32] and indicate similar net donor properties[33] (Scheme 4).



Scheme 4. Formation of phosphanylglycine $W(CO)_5$-complexes.

Whether metal phosphanylglycinate salts and PO⁻-chelate complexes with anionic phosphanylglycinate ligands are more stable than the κ^1P–$W(CO)_5$ coordinated COOH-acidic complexes **11** and comparable to neutral PO⁻- phosphanylacetate chelate complexes is not yet clear and requires further investigations. Nevertheless, the presence of the same P–C–C(O)O structure motif and the importance of the phosphanylacetate nickel catalysts in the Shell Higher Olefin Process[13,14] inspired us to test the suitability of the phosphanylglycines for generation of Ni-catalysts for ethylene oligomerization. A variety of the new compounds was reacted with $Ni(COD)_2$ in THF or toluene (0–20 °C). The in situ generated yellow to brown complex solutions were then transferred into an autoclave and heated under pressure with ethylene (40–50 bar). All *N*-alkyl substituted phosphanylglycines that were screened in the batch oligomerization (**1a**,**c**,**d**,**f**) formed catalysts under these conditions which became active when reaching 80–100 °C (after ca. 15–20 min). The activity was low in the case of the small *N*-propyl substituent but high with bulkier groups such as *t*Bu, *n*Hex and benzhydryl (Table 1 entries 1–6, Fig. 1). The latter might hinder interfering interactions of the *N*-donor atom with the catalyst metal.



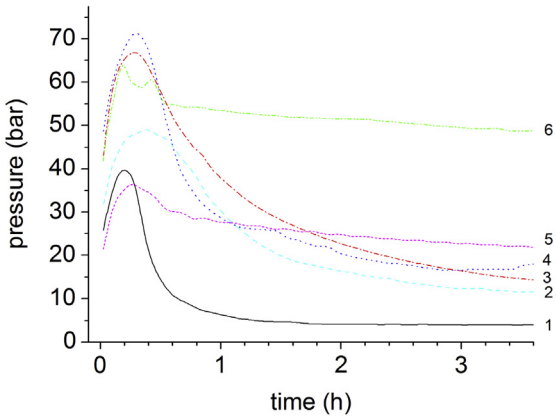


Fig. 1. Pressure-time plots of ethylene oligomerization catalyzed by a) **1c/Ni** in THF (1), b) **1c/Ni** in toluene (3), c) **1d/Ni** in toluene (4), d) **1f/Ni** in toluene (2), e) **1c/Ni** in toluene/1-hexene (6), f) **10c/Ni** in THF (5).

In THF the conversion was faster than in toluene as demonstrated for **1c/Ni** by the more rapid pressure decrease (Fig. 1 curve 1 versus 3). The *N*-primary *n*-hexyl and *N*-secondary benzhydryl substituted catalysts **1d/Ni** and **1f/Ni** worked slightly faster than **1c/Ni** in toluene and the major part of the ethylene was converted within 1 h. The *N*-2-(pyrid-2-ylethyl) and *N*-8-chinolyl substituted

Table 1
Oligomerization of ethylene by in situ formed phosphanylglycinate nickel catalysts

Entry	Ligand, L/Ni (mmol); P_{start} (bar), T (°C), t (h)	C_2H_4 (g, mmol); solvent (mL)	C_2H_4 conversion g (%), TON (mol/mol·h); lower oligomers[a]	Wax (g);[b] mp. (°C); d (g/cm³)	M_{NMR} [g/mol];[c] Vin/int. C=C; Me/C=C
1	**1a**, 0.10/0.10; 40, 100, 16	11.2 (399); THF 20	1.0 (9), 356; C4 38, C6 39, C8 15, C10 2; C12<1	0	—
2	**1c**, 0.11/0.12; 31, 100, 15	8.1 (289); THF 20	6.9 (85), 2240; C4 30, C6 43, C8 19, C10 8	5.2; 113–117; 0.96	1230; 93:7; 1.5
3	**1c**, 0.10/0.11; 50, 100, 16	14.1 (503); toluene 20	12.4 (88), 4420; n.d.	10.6; 115–118; 0.94	900; 90:10; 1.3
4	**1d**, 0.14/0.14; 50, 100, 15	15.1 (538); toluene 20	13.2 (87), 3360; C4 17, C6 24, C8 24, C10 21, C12 12	9.8; 98–100; 0.94	510; 93:7; 1.3
5	**1f**, 0.10/0.10; 30, 100, 15	7.8 (278); toluene 20	6.8 (87), 2420; C4 15, C6 23, C8 19, C10 17, C12 11	6.0; 118–120; n.d.	1240; 95:5; 1.5
6	**1f**, 0.12/0.12; 50, 100, 15	14.1 (503) toluene 20	13.4 (95), 3980; C4 26, C6 25, C8 18, C10 15; C12	10.4; 101–104; n.d.	n.d.
7	**1g**, 0.1/0.1; 40, 100, 15	12.1 (431); THF 20	2.1 (17), 750; C4 17, C6 26, C8 17, C10 4, C12 1[d]	0.3; 99.5; -	390; 90:10; 1.3
8	**1i**, 0.1/0.1; 40, 100/16	11.9 (424); THF 20	1.0 (8), 356; n.d.	0	—
9	**4c**, 0.10/0.11; 50, 100, 15	14 (500); toluene 20	0 (inactive)	—	—
10	**10c**, 0.12/0.13; 29, 100, 15	7.6 (271); THF 20	3.9 (51), 1160; n.d.	3.2; 119–120; 0.96	1250; 96:4; 1.5
11	**1c**, 0.14/0.14; 50, 100, 15	12.2 (435); toluene 10/1-hexene 10	3.4 (28), 866; n.d.	0.6; 40–50; —	n.d.
12	**1c**, 0.12/0.12: 50, 100, 15	12 (430); THF 15, H_2O 5	0 (inactive)	—	—

[a] Solvent and lower α-olefins were separated by flash-distillation (C4 partially lost); oligomer distribution in flash distillate determined by GC (% of C_{2n} by peak areas).
[b] For purification of the remaining wax, see exp. section.
[c] NMR spectra measured after swelling (24 h, 100 °C) in C_6D_5Br at 100 °C; M_{NMR} calculated from integral ratios of proton CH_2/2 and CMe_3/3 signals relative to Vin/3 and CH=CH/2 proton signals; α-to intern olefin and Me/C=C ratios determined by proton integration.
[d] Unknown component (35%) with GC-retention time close to that of toluene.

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phosphanylglycines **1g** and **1i**, which at least in principal are able to form six- and five-membered NN–Ni chelate rings, respectively, gave only marginal conversion (entries 7,8) and led to deactivation of the catalysts after a short time. Screening of the decarboxylation product **4c**, which did not form a catalyst, underlines the crucial role of the COO group (entry 9), and that despite the easy thermal decarboxylation of the 'free' *N*- or *COO*-protonated phosphanylglycines the Ni complex catalysts must be much more thermally stable. A similar strong increase in thermal stability to decarboxylation is known for diphenylphosphanylacetates compared to diphenylphosphanylacetic acid.[23] The borane-protected phosphanylglycine **10c** forms an oligomerization catalyst with $Ni(COD)_2$ but the conversion and reaction rate were considerably lower than in the absence of the borane (entry 10, Fig. 1 curve 5). A test for cooligomerization of ethylene with 1-hexene in toluene solution failed and caused low conversion of ethylene (entry 11, curve 6). The presence of water prevented ethylene conversion (entry 12), possibly by hydrolytic cleavage of the ligand.

The selectivity for formation of relatively short linear α-olefin oligomers with methyl and vinyl ends, analyzed by NMR spectra of swollen oligomers in C_6D_5Br at 100 °C, is very similar to that reported for diphenylphosphanylacetate nickel catalysts.[13,14] Therefore, a similar mechanism can be assumed for the oligomerization, chain start with square planar hydrido- and chain growth with alkyl-nickel(II) PO^--chelate catalysts with the olefin coordinated in *trans*-position to phosphorus and stabilization by the phosphanylacetate backbone. The chain growth is terminated by β-hydride elimination, which provides the NiH catalyst for the next catalytic cycle. The similar working *o*-phosphanylphenolate PONi catalysts with *o*-phenylene-P,O backbone, also studied in our group, were more tolerant to water and stabilized by α-olefins and/or partially incorporating them into the polymer chain[34] but were less easily accessible than the phosphanylglycine Ni catalysts presented here.

2.3. Structural aspects

The structure elucidation of the phosphanylglycines was based on conclusive solution NMR data and for **1b** and **1h** additionally on crystal structure analysis. Most characteristic is the doublet of the α-methine ^{13}C nuclei, P–^{13}CHN, allowing to distinguish zwitterionic *N*-alkyl (δ=60–65) and heterocyclic *N*- or *COO*-protonated *N*-heteroaryl-diphenylphosphanylglycines (δ=54–60) from phosphanylglycolates (PCHO, δ=70–75) by different δ ranges, from decarboxylated PCH_2-moieties by opposite signal amplitudes in the DEPT135 carbon NMR spectra, and from coordinated phosphanyl-, phosphonium- or oxidized (thio)phosphinoyl phosphorus species by different ranges of $^1J_{PC}$ coupling constants. The one-bond P–C coupling constants of the *N*-alkyl phosphanylglycines **1a**–**g** amount to $^1J_{PC}$=12.3–16.5 Hz in the aprotic donor solvent [D_8]THF while these couplings are somewhat larger in the protic solvent CD_3OD (ca. 28 Hz) and for the *N*-heteroaryl substituted compounds **1h**–**l** ($^1J_{PC}$=18.9–25.2 Hz in [D_8]THF). The P–C_α coupling constants of the BH_3- and $W(CO)_5$-coordinated compounds **10c** ($^1J_{PC}$=24.4) and **11c,i** ($^1J_{PC}$=26.1, 16.6) were found in the same range whereas the values for diphenylphosphonium species **3** ($^1J_{PC}$=51.3–57.1 Hz[18]), thiophosphinoyl and phosphinoyl derivatives **7c** ($^1J_{PC}$=39.7 Hz), **7g** ($^1J_{PC}$=59.3 Hz) and **5c** ($^1J_{PC}$=69.7 Hz) are considerable larger. A similar trend was observed for the $^1J_{PC}$ coupling constants of the *i*-phenyl carbon nuclei. Because of the asymmetric α-carbon atom, the two phenyl groups are diastereoisotopic and give rise to each two sets of phenyl signals. The proton signals are likewise indicative but the ranges of the PCH proton signals of phosphanylglycines and –glycolates are less clearly separated than the respective carbon signals, and the PCH proton signals disappear in CD_3OD by H-D exchange. The ^{31}P signals alone do not prove the structure, but the different ranges of the phosphorus resonances of **1** (δ=−2.2–3.1), **2** (δ=4.3–9), **3** (δ=26–28, two signals for *rac*- and *meso*-isomers[18]), **4** (δ=−16.6 to −18.4) and of coordinated phosphanylglycines (**10c** δ=25.8, **11c** δ=26.7, **11i** δ=28.7) or oxidation products (**5c** δ=30.5, **7c** δ=51.5, **7g** δ=43.9) make them ideal markers for reaction monitoring.

More information on the structures of the phosphanylglycines in the solid state is provided by single-crystal structure analyses of the MeOH solvates of racemic **1b** and **1h** (Figs. 2 and 3), grown from their concentrated solutions in methanol. For the methanol solvate of **1a** the diffraction data were insufficient for detailed refinement. The crystals are monoclinic and contain each four molecules in the unit cell. The *N*-alkyl compounds **1a** and **1b** are zwitterionic with methanol bound by hydrogen bond at the COO^- group. Further inter- and intramolecular hydrogen bonds exist, as shown for **1b** in Fig. 4. The *N*-heteroaryl-substituted **1h** exhibits free amino and COOH groups. Bond lengths and angles of **1b** and **1h** display normal values. While the C–N bond lengths and C–N–C angles in **1b** correspond to sp^3 hybridization of the nitrogen atom, the short N1–C3 bond length and the C1–N1–C3 angle of 122.1(2) indicate that the amino-*N*-atom in **1h** is sp^2 hybridized. In combination with the small dihedral angle C1–N1–C3–C4 (4.776(4)°) this allows for stabilization by conjugation of the amino group with the *N*-heterocyclic π-system. The planar phenyl groups at the pyramidal PC3 fragment are twisted to each other to adopt the energetically most suitable conformation.

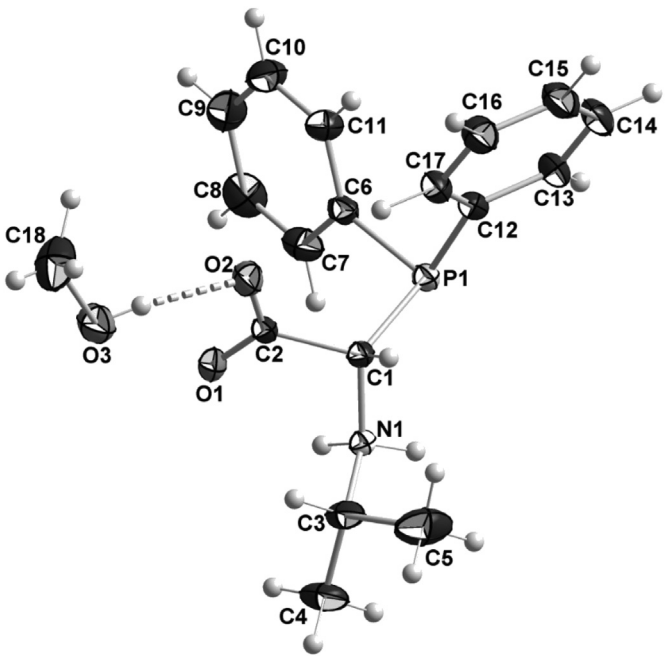

Fig. 2. Molecular structure of the *S*-enantiomer of racemic **1b 1.43 HOCH$_3$** in the crystal (thermal displacement ellipsoids with 50% probability, disordered, non-coordinated methanol molecule omitted for clarity). Selected bond lengths (Å) and angles (deg): P1–C1 1.890(2), P1–C6 1.834(2), P1–C12 1.834(2), C1–N1 1.494(2), N1–C3 1.510(2), C1–C2 1.540(2); C1–P1–C12 101.38(7), C1–P1–C6 103.62(7), C6–P1–C12 104.04(7).

3. Conclusions

N-Secondary diphenylphosphanylglycines with a wide variety of *N*-substituents from primary, secondary or tertiary alkyl to *N*-heteroaryl groups are available by a convenient one-pot three-component reaction of diphenylphosphane, the corresponding primary amine and glyoxylic acid hydrate in a 1:1:1 molar ratio at room temperature in diethyl ether, in some cases, in methanol. The *N*-alkyl compounds are zwitterionic while the *N*-heteroaryl derivatives bear free amino and COOH groups. The reaction proceeds

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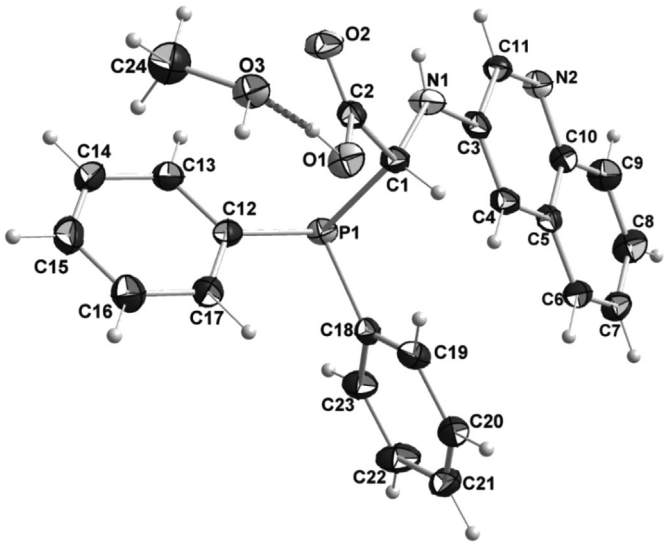

Fig. 3. Molecular structure of the *R*-enantiomer of racemic **1h HOCH$_3$** in the crystal (thermal displacement ellipsoids with 50% probability). Selected bond lengths (Å) and angles (deg): P1–C1 1.923(2), P1–C12 1.831(2), P1–C18 1.832(2), C1–N1 1.440(2), N1–C3 1.367(2), C1–C2 1.498(2); C1–P1–C18 101.84(8), C12–P1–C18 103.30(8), C1–P1–C12 104.56(8).

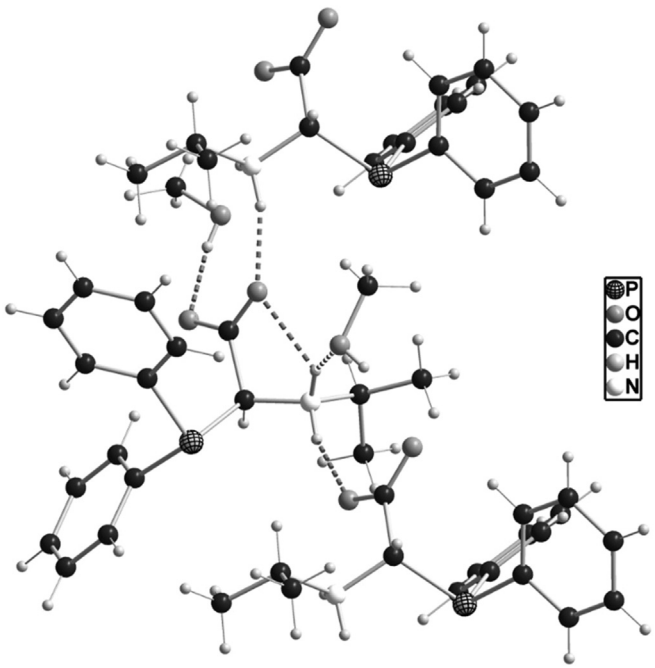

Fig. 4. Inter- and intramolecular hydrogen bonds (dashed lines) within and between the molecules within crystals of **1b 1.43 HOCH$_3$**.

via organoammonium diphenylphosphanylglycolates, which, except for very bulky or very strongly electron withdrawing *N*-substitutents, undergo further condensation to the title compounds. *N*-Primary and *N*-tertiary diphenylphosphanylglycines could not yet be obtained. Heating cannot be used to enforce the condensation because of easy thermal cleavage of CO_2. The electron-lone pair at phosphorus, despite a much weaker base to protons than the amino group, make the title compounds susceptible to various cleavage reactions and lowers the stability of the diphenylphosphanylglycines considerably compared to classic α-amino acids. The blockage of the P-lone pair by coordination of other electrophiles, e.g. BH_3, sulfur or transition metal fragments, which lends the phosphanyl group some electron withdrawing phosphonium character, may increase the susceptibility towards thermal decarboxylation as known from triphenylphosphonio glycolates.[1b,35] With this background it was surprising that heating of a variety of diphenylphosphanylglycines with $Ni(COD)_2$ in the presence of ethylene furnished medium to highly active ethylene oligomerization catalysts. The high selectivity for formation of linear α-olefins with methyl and vinyl end groups is the same as that observed in the oligomerization with nickel diphenylphosphanylacetate chelate complexes, suggesting that the catalysts are structurally related and that the still unexplored P-coordinated transition metal diphenylphosphanyl glycinates may be more stable and useful also for other transition metal catalyzed organic transformations. The description of the synthetic access and the properties of the title compounds paves the way for such studies.

4. Experimental

4.1. General

All operations were carried out under nitrogen by using Schlenk techniques. Solvents were dried and distilled before use. Diphenylphosphane was synthesized by cleavage of a phenyl group from triphenylphosphane with sodium in liquid ammonia and neutralization with excess NH_4Cl.[36] Other chemicals were used as purchased after degassing in an ultrasound bath under nitrogen. Solutions of glyoxylic acid hydrate (GAH) in diethyl ether were prepared in an ultrasound bath without heating. NMR spectra were recorded on multinuclear FT-NMR spectrometers ARX300 or Avance II (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Chemical shifts δ are given in ppm and refer to tetramethylsilane for ^{1}H and ^{13}C and to H_3PO_4 (85%) for ^{31}P or to solvent signals referenced to these standards. Assignments for phenyl nuclei are denoted by *i*, *o*, *m* and *p*, those of *N*-alkyl groups by α, β etc. and of additional phenyl groups by *i*′, *o*′, *m*′ and *p*′; for assignment numbers in heterocyclic substituents see Scheme 1. Coupling constants refer to J_{HH} (^{1}H NMR) or J_{PC} (^{13}C NMR) unless stated otherwise. Satellite signals are abbreviated as satl. ^{31}P integral or signal height ratios refer to AQ=0.33 s and *D*1=2.0 s and are not strictly quantitative. Longer NMR measurements were carried out in melt closed NMR tubes. (Plastic caps proved to be not air-tight and led to slow oxidation of air sensitive phosphanylglycines and formation of product mixtures.) Melting ranges (thermal decomposition) were determined with a Sanyo Gallenkamp melting point apparatus, elemental analysis with a CHNS-932 analyzer from LECO using standard conditions.

4.2. Three-component synthesis of *N*-substituted diphenylphosphanylglycines

*4.2.1. Diphenylphosphanyl(propylamino)acetic acid (**1a**).* Glyoxylic acid hydrate (0.50 g, 5.43 mmol) was dissolved in diethyl ether (7 mL) and added at room temperature to a solution of Ph_2PH (1.0 g, 5.37 mmol) and *n*-propylamine (0.44 mL, 5.35 mmol) in diethyl ether (15 mL). Precipitation started after few minutes. After stirring overnight (≈15 h) the mixture was separated, the precipitate washed with diethyl ether and dried under vacuum to yield 1.2 g (74%) of **1a** as white powder. Crystallization from methanol furnished colorless needles of **1a**·MeOH, mp. 85–92 °C (dec). Figure with crude structure in the crystal see Supplementary data. Anal. Calcd for $C_{17}H_{20}NO_2P\cdot CH_3OH$ (333.36): C, 64.85; H, 7.26; N, 4.20. Found: C, 64.57; H, 7.31; N, 4.19. ^{1}H NMR ([D$_8$]THF): δ=0.86 (t, ^3J=7.4 Hz, 3H, CH_3), 1.43 (qd, ^3J=7.2, $^5J_{PH}$=3.8 Hz, 2H, CH_2), 2.45 (dt, ^2J=11.0, ^3J=7.1 Hz, 1H, NCH_A), 2.65 (dt, ^2J=11.0, ^3J=6.9 Hz, 1H, NCH_B), 4.00 (d, $^2J_{PH}$=2.8 Hz, 1H, PCH), 4.8 (vbr s, 3H, 2 OH, NH), 7.22–7.32 (m, 6H, Ph), 7.40–7.60 (m, 4H, Ph); 3.26 (s, 3H, MeOH). ^{13}C{^{1}H} and

DEPT-135 NMR ([D$_8$]THF): δ=12.09 (CH_3), 23.97 CH_2), 52.08 (d, ^3J=8.4 Hz, NCH_2), 63.59 (d, ^1J=13.9 Hz, PCH), 128.64 (d, ^3J=6.1 Hz, 2 *m*-CH_A), 128.73 (d, ^3J=8.3 Hz, 2 *m*-CH_B), 129.25 (*p*-CH_A), 129.84 (*p*-CH_B), 133.76 (d, ^2J=17.2 Hz, 2 *o*-CH_A), 135.45 (d, ^2J=21.2 Hz, 2 *o*-CH_B), 133.79 (d, ^1J=17.8 Hz, *i*-C_{qA}), 133.91 (d, ^1J=18.2 Hz, *i*-C_{qB}), 173.96 (noise level, d, ^2J=9.1 Hz, COO); 49.84 (MeOH). $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ_A=−0.8.

*4.2.2. Diphenylphosphanyl(isopropylamino)acetic acid (**1b**).* A solution of Ph_2PH (1.0 g, 5.37 mmol) and isopropylamine (0.46 mL, 5.40 mmol) in diethyl ether (10 mL) was added at room temperature to an ethereal solution of GAH (0.50 g, 5.43 mmol). Stirring for 24 h provided a white precipitate, which was separated by filtration, was washed twice with diethyl ether and dried in vacuum, yielding 1.4 g (85%) of **1b** as white powder. Anal. Calcd for $C_{17}H_{20}NO_2P$ (301.32): C, 67.76; H, 6.69; N, 4.65. Found: C, 67.76; H, 6.73; N, 4.61. Compound **1b** was easily soluble in methanol and crystallized in form of less soluble colorless needles of **1b**·MeOH, mp. 93–101 °C (dec). Crystal data are compiled in Table 2, selected bond lengths and angles in Fig. 2. **1b**. IR (KBr): ν=3502 (vst, OH), 3386 (st), 2651 (m), 2525 (m), 2409 (m), ca. 1640 (sh), 1615 (vst) cm^{-1}. **1b**·MeOH−^{1}H NMR ([D$_8$]THF): δ=0.98 (d, ^3J=6.2 Hz, 6H, CH_3), 2.76 (hept d, ^3J=6.2, $^4J_{PH}$=0.7 Hz, 1H, CH), 4.15 (d, $^2J_{PH}$=3.1 Hz, 1H, PCH), 4.4–5.6 (sbr, 2H, OH, NH), 7.23–7.33 (m, 6H, Ph), 7.47–7.62 (m, 4H, Ph); 3.26 (s, 3H, MeOH). $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ=22.13, 24.05 (CH_3), 49.18 (d, ^3J=9.2 Hz, NCH), 61.20 (d, ^1J=14.1, PCHN), 128.64, 128.74 (superimposed doublets, ^3J=6.5, 8.0 Hz, 2 *m*-CH_A, 2 *m*-CH_B), 128.98 (*p*-CH_A), 129.94 (*p*-CH_B), 133.75 (d, ^2J=17.4 Hz, two *o*-CH_A), 135.54 (d, ^2J=21.4 Hz, 2 *o*-CH_B), 136.99 (d, ^1J=14.6 Hz, *i*-C_{qA}), 138.14 (d, ^1J=18.1 Hz, *i*-C_{qB}), 174.03 (d, ^2J=12.8 Hz, COO); 49.85 (MeOH). $^{31}P\{^1H\}$ NMR in [D$_8$]THF δ=−0.2; in CD_3OD δ=−1.9.

*4.2.3. tert-Butylamino(diphenylphosphanyl)acetic acid (**1c**).* A solution of GAH (0.50 g, 5.43 mmol) in diethyl ether (10 mL) was added to a solution of Ph_2PH (1.0 g, 5.37 mmol) and *tert*-butylamine (0.56 mL, 5.34 mmol) in diethyl ether (20 mL). Precipitation started immediately. NMR monitoring of a sample filtered after 10 min displayed the phosphorus resonance in CD_3OD solution at δ=8.0 (in [D$_8$]THF δ=6.5), corresponding to **2c**.[18b] After stirring for 24 h the precipitate was filtered, washed with diethyl ether and dried under vacuum. Crystallization from a small amount of methanol furnished 1.50 g (83%) colorless needles of **1c**·MeOH. Anal. Calcd for $C_{18}H_{22}NO_2P\cdot CH_3OH$ (347.40): C, 65.69; H, 7.54; N, 4.03. Found: C, 65.39; H, 7.57; N, 3.93. IR (KBr): ν=3378 (st), 2981 (st), 2874 (m), 2482 (m), 1643 (vst) cm^{-1}. ^{1}H and CH–COSY NMR ([D$_8$]THF, ref. THF δ 1.72): δ=0.95 (s, 9H, CMe_3), 4.11 (d, $^2J_{PH}$=2.7 Hz, 1H, CH), 4.4–5.2 (s br, 3H, OH, NH), 7.22–7.32 (m, 6H, Ph), 7.41–7.48 (m, 2H, Ph), 7.53–7.61 (m, 2H, Ph); 3.26 (s, 3H, MeOH). $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ=29.39 (s, CH_3), 52.47 (d, ^3J=9.3 Hz, CMe_3), 58.09 (d, ^1J=12.3 Hz, PCH), 128.41 (d, ^3J=5.5 Hz, 2 *m*-CH_A), 128.55 (d, $^3J_{PC}$=7.6 Hz, 2 *m*-CH_B), 129.00 (s, 2 *p*-CH), 134.21 (d, ^2J=18.3 Hz, 2 *o*-CH_A), 135.58 (d, ^2J=21.3 Hz, 2 *o*-CH_B), 136.80 (d, ^1J=17.2 Hz, *i*-C_{qA}), 138.10 (d, ^1J=18.1 Hz, *i*-C_{qB}), 175.83 (d, ^2J=12.4 Hz, COOH); 49.76 (MeOH). $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ=3.1. MS (EI, 70 eV, 260 °C): *m/z* (%)=315 (7) [M$^+$], 270 (0.5) [M$^+$−COOH], 187 (43), 186 (68) [Ph_2PH^+], 185 (44), 183 (53), 108 (38), 107 (81), 106 (71), 84 (25), 75 (100).

During longer NMR measurement or storage of the solution in [D$_8$]THF at 22–25 °C **1c**·MeOH underwent slow decarboxylation, indicated by formation of **4c** (15, 40, 57% after 3 h, 1 d, 7 d by integration of ^{31}P signals). In $CDCl_3$ solution the decarboxylation was faster (ca. 70% during sample preparation and slight warming for dissolution). **4c**−^{1}H NMR ($CDCl_3$, 7.27): δ=1.08 (s, 9H, CMe_3), 3.31 (d, $^2J_{PH}$=1.4 Hz, 2H, PCH_2N), 7.28 (br, evtl. NH), 7.32–7.37 (m, 6H, Ph), 7.43–7.60 (m, 4H, Ph). $^{13}C\{^1H\}$ and DEPT-135 NMR ($CDCl_3$): δ=28.52 (s, CMe_3), 42.54 (d, ^1J=4.6 Hz, NCH_2), 51.65 (d, ^3J=10.5 Hz, CMe_3), 128.45 (^3J=6.2 Hz, *m*-CH), 128.70 (*s*, *p*-CH), 132.86 (d, ^2J=18.5 Hz, *o*-CH), 137.41 (d, ^1J=13.3 Hz, *i*-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=−16.6. These NMR data are in good accordance with those of **4c**, prepared from Ph_2PCH_2OH and *t*$BuNH_2$.[37] Air oxidation led slowly

Table 2
Crystal and structure refinement data for **1b**·1.43MeOH and **1h**·MeOH. **1b**·1.43MeOH contains two crystallographic sites, which are occupied with methanol molecules. One position is fully occupied. The methanol molecules on this site are connected with **1b** by hydrogen bonds while the other site is not fully occupied and the methanol molecule is disordered and does not form hydrogen bonds

	1b	**1h**
Empirical formula	$C_{18.43}H_{25.72}NO_{3.43}P$	$C_{24}H_{23}N_2O_3P$
Formula weight	347.13	418.41
Temperature	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions	*a*=12.7797(9) Å	*a*=9.2122(4) Å
	b=9.9828(6) Å	*b*=11.4288(4) Å
	β=96.112(4)°	β=90.505(1)°
	c=15.0121(9) Å	*c*=19.9939(8) Å
Volume	1904.3(2) Å^3	2105.06(1) Å^3
Z	4	4
Density (calculated)	1.220 g/cm^3	1.320 g/cm^3
Absorption coefficient	0.162 mm^{-1}	0.159 mm^{-1}
F(000)	750	880
Crystal size	0.58×0.41×0.39 mm^3	0.15×0.07×0.06 mm^3
Theta range for data collection	2.21–27.95°	2.71–28.26°
Index ranges	−16 ≤ *h*<=16,	−12 ≤ *h*<=12,
	−13 ≤ *k*<=12,	−15 ≤ *k*<=12,
	−19 ≤ *l*<=19	−26 ≤ *l*<=25
Reflections collected	34,165	18,663
Independent reflections	4562 [R(int)=0.0362]	5213 [R(int)=0.0559]
Absorption correction Max. and min transmission	Multiscan (SADABS) 0.9394 and 0.9117	0.9905 and 0.9765
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4562/0/225	5213/0/287
Goodness-of-fit on F^2	1.043	0.980
Final R indices [I>2sigma(I)]	*R*1=0.0464, wR2=0.1208	*R*1=0.0469, wR2=0.0921
R indices (all data)	*R*1=0.0635, wR2=0.1289	*R*1=0.0963, wR2=0.1028
Largest diff. peak and hole	0.744–0.528 e·Å^{-3}	0.329–0.297 e·Å^{-3}

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to $Ph_2P(O)CH_2NHtBu$, ^1H NMR($CDCl_3$): δ=1.07 (*t*Bu), 3.40 (d, $^2J_{PH}$=9.9 Hz, PCH_2N), 7.20–7.87 (m, 10H, Ph); ^{31}P NMR ($CDCl_3$): δ=31.1.

*4.2.4. Diphenylphosphanyl(n-hexylamino)acetic acid (**1d**).* A solution of GAH (500 mg, 5.43 mmol) in diethyl ether (10 mL) was added to a solution of Ph_2PH (1.0 g, 5.37 mmol) and *n*-hexylamine (0.70 mL, 0.54 g, 5.34 mmol) in diethyl ether (20 mL). An initial precipitate dissolved rapidly. The product precipitated slowly (2 d, ca. 20 °C), was filtered, washed with ether and dried under vacuum, yield 1.6 g (82%) of white powder. Compound **1d** was sparingly soluble in THF or $CDCl_3$ and decomposed on heating in these solvents, but it was easily soluble in CD_3OD. Crystallization from a small amount of methanol provided a methanol solvate **1d**·MeOH, mp. 104–108 °C (dec), which was also soluble in [D_8]THF. **1d**: Anal. Calcd for $C_{20}H_{26}NO_2P$ (343.40): C, 69.95; H, 7.63; N, 4.08. Found: C, 70.39; H, 7.44; N, 3.96. **1d**·MeOH–^1H NMR ([D_8]THF): δ=0.87 (m, 3H, CH_3), 1.20–1.48 (m, 8H, CH_2), 2.48 (dt, ^2J=11.0, ^3J=6.7 Hz, 1H, NCH_A), 2.68 (dt, ^2J=11.0, ^3J=6.7 Hz, 1H, NCH_B), 4.00 (d, $^2J_{PH}$=2.9 Hz, 1H, PCH), 7.22–7.32 (m, 6H, Ph), 7.42–7.60 (m, 4H, Ph); 3.26 (s, 3H, MeOH), NH, OH (vbr). $^{13}C\{^1H\}$ NMR ([D_8]THF): δ=14.40 (CH_3), 23.53 (CH_2), 27.82 (CH_2), 30.88 (CH_2), 32.67 (CH_2), 50.14 (d, ^3J=8.9 Hz, NCH_2), 63.60 (d, ^1J=15.2 Hz, PCH), 128.65 (d, ^3J=6.5 Hz, *m*-C_A), 128.75 (d, ^3J=8.0 Hz, *m*-C_B), 128.99 (*p*-C_A), 129.86 (*p*-C_B), 133.80 (d, ^2J=17.5 Hz, *o*-C_A), 135.45 (d, ^2J=21.3 Hz, *o*-C_B), 173.8 (d, $^2J\approx$9 Hz, COO, noise level); *i*-C_q at noise level, 49.85 (MeOH). $^{31}P\{^1H\}$ NMR ([D_8]THF): δ=–0.7. ^1H NMR (CD_3OD): δ=0.99 (m, 3H, Me), 1.32–1.36 (m, 6H, 3 CH_2), 1.64 (m, 2H, CH_2), 3.00 (td, ^3J=8.0, $^4J_{PH}$=0.6 Hz, 2H, NCH_2), 4.38 (br s, 0.9H, PCH), 7.28–7.35, 7.42–7.50 (m, 13H, Ph, OH, NH). $^{13}C\{^1H\}$ NMR and DEPT-135 (CD_3OD): δ=14.26 (CH_3), 23.45, 27.13, 27.34, 32.39 (CH_2), 49.75 (NCH_2), 64.90 (d, ^1J=28.1 Hz, PCH), 129.37 (d, ^3J=7.9 Hz, *m*-CH_A), 129.98 (d, ^3J=7.9 Hz, *m*-CH_B), 130.56 (*p*-CH_A), 131.02 (*p*-CH_B), 135.07 (d, ^2J=20.6 Hz, *o*-CH_A), 135.49 (d, ^2J=22.3 Hz, *o*-CH_B), 169.76 (COO); *i*-C_q at noise level. $^{31}P\{^1H\}$ NMR (CD_3OD): δ=–2.2.

*4.2.5. Diphenylphosphanyl(2-methoxybenzylamino)acetic acid (**1e**).* A solution of Ph_2PH (1.0 g, 5.37 mmol) and (2-methoxyphenyl) methylamine (0.74 g, 5.39 mmol) in diethyl ether (10 mL) was added at room temperature to a solution of GAH (0.50 g, 5.43 mmol) in diethyl ether. After stirring for 24 h the precipitate was separated, washed with ether and dried to give 1.11 g (54%) white powder. Crystallization from MeOH afforded colorless needles of **1e**·0.6 MeOH. Anal. Calcd for $C_{22}H_{22}NO_3P\cdot0.6\ CH_3OH$ (398.62): C, 68.10; H, 6.17; N, 3.54. Found: C, 67.85; H, 5.74; N, 3.51. IR (KBr): ν=3540 (st, OH), 3058 (m), 2956 (m), 2496 (m), 1641 (vst), 1364 (st), 1250 (st), 750 (st) cm^{-1}. ^1H NMR ([D_8]THF): δ=3.68 (d, ^2J=13.2 Hz, 1H, NCH_{2A}), 3.73 (s, 3H, OMe), 3.83 (d, ^2J=13.2 Hz, 1H, NCH_{2B}), 4.07 (d, $^2J_{PH}$=1.8 Hz, 1H, PCH), 5.32 (br s, 2.6H, NH_2, 0.6 OH), 6.77–6.86 (m, 2H, 3-H, 5-H), 7.10–7.32 (m, 8H, 4-H, 6-H, Ph), 7.42–7.55 (m, 4H, Ph); 3.26 (s, 2H, 0.6 MeOH). $^{13}C\{^1H\}$ and DEPT-135 NMR ([D_8]THF): δ=48.70 (d, ^3J=8.5 Hz, CH_2), 55.40 (s, 2-OCH_3), 62.92 (d, ^1J=15.5 Hz, PCH), 110.78 (3-CH), 120.81 (s, 5-CH), 128.66 (d, ^3J=6.2 Hz, 2 *m*-CH_A), 128.70 (superimp. s, 4- or 6-CH), 128.75 (d, ^3J=6.9 Hz, 2 *m*-CH_B), 128.96 (1-C_q), 129.02 (s, 4- or 6-CH), 129.68 (*p*-CH_A), 130.30 (*p*-CH_B), 134.08 (d, ^2J=18.4 Hz, 2 *o*-CH_A), 135.23 (d, ^2J=20.6 Hz, 2 *o*-CH_B), 137.15 (d, ^1J=15.9 Hz, *i*-C_{qA}), 137.80 (d, ^1J=18.3 Hz, *i*-C_{qB}), 158.64 (2-C_q), 173.73 (d, ^2J=9.4 Hz, COOH); 49.84 (0.6 MeOH). $^{31}P\{^1H\}$ NMR ([D_8]THF): δ=–0.2.

*4.2.6. Benzhydrylamino(diphenylphosphanyl)acetic acid (**1f**).* A solution of GAH (403 mg, 4.38 mmol), dissolved in diethyl ether (10 mL), was added to a solution of Ph_2PH (815 mg, 4.38 mmol) and Ph_2CHNH_2 (0.76 mL, 4.38 mmol) in diethyl ether (20 mL). A sticky precipitate initially formed dissolved during stirring overnight. The solvent and water was removed in vacuum. The remaining foam was washed with hexane, and the residue crystallized from methanol. Drying under vacuum gave 1.7 g (91%) white solid, mp. 121–122 °C (dec). Anal. Calcd for $C_{27}H_{24}NO_2P$ (425.47): C, 76.22; N, 3.29. Found: C, 76.34; N, 3.33. ^1H NMR ([D_8]THF): δ=3.98 (d, $^2J_{PH}$=2.4 Hz, 1H, PCH), 4.86 (s, 1H, NCH), 7.05–7.35 (m, 16H, Ph), 7.45–7.55 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ([D_8]THF): δ=60.61 (d, ^1J=16.5 Hz, PCH), 67.15 (d, ^3J=9.8 Hz, NCH), 127.54, 127.74 (2 *p*-CH, Ph_2C), 127.77, 128.85, 128.91, 128.96 (2 *o*- and 2 *m*-C, Ph_2C), 128.66 (d, ^3J=7.3 Hz, *m*-C_A), 128.73 (d, ^3J=6.6 Hz, *m*-C_B), 129.40 (*p*-C_A), 129.74 (*p*-C_B), 134.41 (d, ^2J=19.3 Hz, *o*-C_A), 135.11 (d, ^2J=21.0 Hz, *o*-C_B), 136.31 (d, ^1J=15.4 Hz, *i*-C_A), 136.75 (d, ^1J=17.3 Hz, *i*-C_B), 143.24, 145.22 (2 *i*-C_q, Ph_2C), 173.56 (d, ^2J=11.4 Hz, COO^-). $^{31}P\{^1H\}$ NMR ([D_8]THF): δ=1.8; storage of the solution led to slow decarboxylation, indicated by slowly increasing signals at δ=–18 and –28.

NMR spectra of a solution of **1f** in $CDCl_3$, prepared with slight warming (30–35 °C), displayed 57%, repeated measurements after 2 d quantitative decarboxylation, leading mainly to **4f**, a minor amount of $(Ph_2PCH_2)_2NCHPh_2$ with very similar ^{31}P and PCH_2 proton chemical shifts as reported for $(Ph_2PCH_2)_2NPh$[38] and a trace of Ph_2PH (80:17:3% by ^{31}P integration). **4f**–^1H NMR ($CDCl_3$): δ=2.2–2.8 (vbr. NH), 3.33 (d, $^2J_{PH}$=3.3 Hz, PCH_2N), 4.97 (br, NCH), 7.10–7.50 (m, 20H, 4 Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=47.89 (d, ^1J=9.1 Hz, PCH_2N), 68.40 (d, ^3J=11.5 Hz, $NCHPh_2$), 127.06 (2 *p*′-CH), 127.39, 128.43 (4 *o*′-CH, 4 *m*′-CH), 128.21 (d, ^3J=7.2 Hz, 4 *m*-CH), 128.69 (2 *p*-CH), 132.95 (d, ^2J=17.4 Hz, 4 *o*-CH), 137.10 (d, ^1J=12.4 Hz, 2 *i*-C_q), 143.8 (2 *i*′-C_q). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=–18.8. $(Ph_2PCH_2)_2NCHPh_2$–^1H NMR ($CDCl_3$): δ=3.75 (br, PCH_2N), Ph superimposed. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=128.21 (d, ^3J=7.2 Hz, *m*-CH), 128.63 (*p*-CH), 133.35 (d, ^2J=18.5 Hz, *o*-CH), 137.7 (d, $^1J\approx$12 Hz, *i*-C_q); (PCH_2N broad, within noise). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=–28.8.

*4.2.7. Diphenylphosphanyl(2-pyrid-2-yl-ethylamino)acetic acid (**1g**).* A solution of GAH (0.35 g, 3.8 mmol) in diethyl ether (7 mL) was added to a solution of Ph_2PH (0.70 g, 3.76 mmol) and 2-(2-pyridyl) ethylamine (0.46 g, 3.76 mmol) in diethyl ether (30 mL). After stirring for 15 h the precipitate was separated, washed with a small amount of ether and dried under vacuum to give 0.90 g (65%) white powder. Crystallization from MeOH furnished the methanol solvate **1g**·MeOH. Anal. Calcd for $C_{21}H_{21}N_2O_2P\cdot CH_3OH$ (396.42): C, 66.66; H, 6.36; N, 7.07. Found: C, 66.71; H, 6.16; N, 7.08. ^1H NMR and H,H–COSY ([D_8]THF): δ=2.80–3.13 (m, 4H, CH_2), 4.04 (d, $^2J_{PH}$=3.0 Hz, 1H, PCH), 5.1 (s br, 3H, NH, OH), 7.06 (ddd, ^3J=7.5, 4.8, ^4J=1.5 Hz, H-5), 7.11 (d, ^3J=7.5 Hz, H-3), 7.17–7.32 (m, 6H, Ph), 7.37–7.47 (m, 2H, Ph), 7.49–7.57 (m, 3H, H-4, Ph), 8.41 (ddd, ^3J=4.8, ^4J=1.5 Hz, 1H, H-6); 3.26 (s, 3H, MeOH). $^{13}C\{^1H\}$ NMR and DEPT-135 ([D_8]THF): δ=39.18 (CH_2), 49.67 (d, ^3J=8.8 Hz, NCH_2), 63.78 (d, ^1J=15.3 Hz, PCHN), 121.55 (3-CH), 123.78 (5-CH), 128.45 (d, ^3J=6.5 Hz, 2 *m*-CH), 128.65 (d, ^3J=7.5 Hz, 2 *m*-CH), 128.81 (*p*-CH), 129.66 (*p*-CH), 133.83 (d, ^2J=18.1 Hz, 2 *o*-CH), 135.32 (d, ^2J=21.1 Hz, 2 *o*-CH), 136.44 (4-CH), 137.13 (d, ^1J=19 Hz, *i*-C_q), 138.0 (d, $^1J\approx$18 Hz, *i*-C_q), 149.80 (6-CH), 161.31 (2-C_q), 173.89 (br, COOH); 49.77 (MeOH). $^{31}P\{^1H\}$ NMR ([D_8]THF): δ=–0.3. (NMR spectra in CD_3OD, indicating H-D exchange from PCH to see Supplementary data.)

*4.2.8. Diphenylphosphanyl(quinolin-3-ylamino)acetic acid (**1h**).* A solution of Ph_2PH (1.0 g, 5.37 mmol) and 3-aminoquinoline (0.78 g, 5.40 mmol) in diethyl ether (10 mL) was added to a solution of GAH (0.50 g, 5.40 mmol) in diethyl ether (10 mL). After stirring for 24 h the precipitate was separated, washed with ether and dried under vacuum to give 1.80 g (86%) yellow powder, mp. 130–135 °C (dec). Anal. Calcd for $C_{23}H_{19}N_2O_2P$ (386.12): C, 71.50; H, 4.96; N, 7.25. Found: C, 71.50; H, 4.66; N, 7.26. Crystallization from methanol furnished yellow crystals of the methanol solvate. Crystal data of **1h**·MeOH are compiled in Table 2, selected bond lengths and angles in Fig. 3. IR (KBr): ν=3415 (st), 3049 (m), 2428 (wm br), 1706 (st)

cm^{-1}. ^{1}H NMR ([D$_8$]THF): δ=4.94 (d, $^2J_{PH}$=9.4 Hz, 1H, PCH), 5.89 (br d, $^3J_{PH}$=9.2 Hz, 1H, NH), 7.04 (d, ^4J=2.8 Hz, 1H, 4-H), 7.14–7.25 (m, 8H), 7.40–7.50 (m, 5H), 7.65–7.72 (m, 1H), 8.38 (d, ^4J=2.8 Hz, 1H, 2-H); 3.15 (s, 3H, MeOH). ^{13}C{^{1}H} NMR ([D$_8$]THF, DEPT-135): δ=57.84 (d, ^1J=18.9 Hz, PCH), 111.32 (s, 4-CH), 125.23, 126.70, 127.17 (3s, 5-CH, 6-CH, 7-CH), 128.92 (d, ^3J=7.0 Hz, 2 *m*-CH$_A$), 129.16 (d, ^3J=6.5 Hz, 2 *m*-CH$_B$), 129.51 (s, *p*-CH$_A$), 129.59 (s, *p*-CH$_B$), 130.21 (s, 8-CH), 130.33 (s, 10-C$_q$), 133.67 (d, ^2J=18.8 Hz, 2 *o*-CH$_A$), 135.25 (d, ^2J=21.2 Hz, 2 *o*-CH$_B$), 135.90 (d, ^1J=15.9 Hz, *i*-C$_{qA}$), 136.81 (d, ^1J=17.2 Hz, *i*-C$_{qB}$), 142.07 (d, ^3J=6.8 Hz, 3-C$_q$), 143.05 (s, 9-C$_q$), 144.44 (s, 2-CH), 171.96 (d, ^2J=9.2 Hz, COOH); 49.78 (MeOH). ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=−0.6.

*4.2.9. Diphenylphosphanyl(quinolin-8-ylamino)acetic acid (**1i**).* A solution of GAH (0.30 g, 3.26 mmol) in diethyl ether (15 mL) was added to a solution of Ph$_2$PH (0.60 g, 3.22 mmol) and 8-aminoquinoline (0.46 g, 3.19 mmol) in diethyl ether (3 mL). The yellow precipitate formed during stirring overnight was separated, washed with ether and dried under vacuum. Crystallization from methanol provided 0.81 g (60%) of the yellow methanol solvate, mp. 125–130 °C (dec). Anal. Calcd for C$_{23}$H$_{19}$N$_2$O$_2$P·CH$_3$OH (418.14): C, 68.89; H, 5.54; N, 6.69. Found: C, 68.88; H, 5.57; N, 6.68. IR (KBr): ν=3415 (st), 3049 (m), 2410 (br), 1705 (st) cm^{-1}. ^{1}H NMR ([D$_8$]THF): δ=5.11 (d, $^2J_{PH}$=9.0 Hz, 1H, PCHN), 6.69 (br d, ^3J=7.4 Hz, 1H, H-7), 7.01 (br dd, *J*=8.8, 1.3 Hz, 1H, NH), 7.03 (dd, ^3J=8.2, ^4J=1.0 Hz, 1H, H-5), 7.22–7.37 (m, 8H, H-3, H-6, Ph), 7.49–7.69 (2m, 4H, Ph), 8.02 (dd, ^3J=8.3, ^4J=1.7 Hz, 1H, H-4), 8.60 (dd, ^3J=4.2, ^4J=1.7 Hz, 1H, H-2); 3.25 (s, MeOH). ^{13}C{^{1}H} and DEPT-135 NMR (D^8-THF): δ=57.41 (d, ^1J=22.2 Hz, PCHN), 106.42 (s, 7-CH), 115.44 (s, 5-CH), 122.13 (s, 3-CH), 128.13 (s, 6-CH), 128.93 (d, ^3J=7.4 Hz, 2 *m*-CH$_A$), 129.14 (d, ^3J=6.5 Hz, 2 *m*-CH$_B$), 129.51 (s, 10-C$_q$), 129.62 (s, *p*-CH$_A$), 129.97 (s, *p*-CH$_B$), 134.12 (d, ^2J=19.3 Hz, 2 *o*-CH$_A$), 134.91 (d, ^2J=20.4 Hz, 2 *o*-CH$_B$), 136.15 or 136.20 (d, ^1J=13.2 or 17.1 Hz, *i*-C$_{qA}$), 136.26 (s, 4-CH), 136.36 or 136.41 (d, ^1J=18.4 or 14.6 Hz, *i*-C$_{qB}$), 139.43 (s, 9-C$_q$), 144.24 (d, ^3J=5.0 Hz, 8-C$_q$), 147.69 (s, 2-CH), 171.71 (d, ^2J=7.9 Hz, COOH); 49.83 (s, MeOH). ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=1.4.

*4.2.10. Diphenylphosphanyl(4-methylpyrid-2-ylamino)acetic acid (**1j**).* A solution of GAH (0.50 g, 5.43 mmol) in diethyl ether (10 mL) was added to a solution of Ph$_2$PH (1.0 g, 5.37 mmol) and 4-methylpyridin-2-ylamine (0.58 g, 5.36 mmol) in diethyl ether (15 mL). Precipitation startet after few minutes. Filtration after stirring overnight, washing the precipitate with ether and drying under vacuum gave 1.60 g (84%) white powder. Anal. Calcd for C$_{20}$H$_{19}$N$_2$O$_2$P (350.35): C, 68.56; H, 5.47; N, 8.00. Found: C, 68.55; H, 5.55; N, 8.11. Crystallization from methanol provided colorless needles of the methanol solvate **1j**·MeOH. ^{1}H NMR ([D$_8$]THF): δ=2.12 (s, 3H, CH$_3$), 5.72 (br s, PCH), 6.29 (d, $^4J\approx$1 Hz, 1H, 3-H), 6.33 (dd, ^3J=5.2, ^4J=0.9 Hz, 1H, 5-H), 7.23–7.32 (m, 6H, Ph), 7.43–7.56 (m, 4H, Ph), 7.82 (d, ^3J=5.2 Hz, 1H, 6-H); 3.25 (s, MeOH). ^{13}C{^{1}H} and DEPT-135 NMR ([D$_8$]THF): δ=20.82 (s, CH$_3$), 54.64 (d, ^1J=20.6 Hz, PCH), 110.08 (s, 3-CH), 115.23 (s, 5-CH), 128.71 (d, ^3J=7.2 Hz, 2 *m*-CH$_A$), 128.86 (d, ^3J=6.6 Hz, 2 *m*-CH$_B$), 129.34 (s, *p*-CH$_A$), 129.56 (s, *p*-CH$_B$), 134.18 (d, ^2J=19.7 Hz, 2 *o*-CH$_A$), 134.76 (d, ^2J=20.1 Hz, 2 *o*-CH$_B$), 136.94 (d, ^1J=17.3 Hz, *i*-C$_{qA}$), 138.88 (d, ^1J=15.6 Hz, *i*-C$_{qB}$), 147.78 (s, 6-CH), 147.92 (s, 4-C$_q$), 158.94 (d, ^3J=4.1 Hz, 2-C$_q$), 172.58 (d, ^2J=10.6 Hz, COOH); 49.75 (s, MeOH). ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=2.4.

NMR spectra of **1j**·MeOH in [D$_8$]THF displayed slow decarboxylation at 25 °C; after measuring for 12 h the ^{13}C NMR spectrum indicates ca. 30% (by CH signal intensities) of **4j**. ^{1}H NMR ([D$_8$]THF): δ=2.14 (s, CH$_3$), 4.09 (d, $^2J_{PH}$=3.9 Hz, PCH$_2$N), 6.5 (vbr, NH), 7.78 (d, ^3J=5.2 Hz, 1H, 6-H); 3-H, 5-H and phenyl proton signals superimposed. ^{13}C{^{1}H} and DEPT-135 NMR ([D$_8$]THF): δ=20.93 (s, CH$_3$), 42.48 (d, ^1J=9.3 Hz, PCH$_2$), 108.89 (s, 3-CH), 114.30 (s, 5-CH), 129.03 (s, 2 *p*-CH), 129.16 (d, ^3J=6.6 Hz, 4 *m*-CH), 133.66 (d, ^2J=18.3 Hz, 4 *o*-CH), 138.88 (d, ^1J=15.6 Hz, 2 *i*-C$_q$), 147.81 (s, 6-CH), 147.9 (s, 4-C$_q$), 159.77 (br, 2-C$_q$). ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=−18.4.

*4.2.11. 2-Pyridylammonium diphenylphosphanyl(hydroxy)acetate (**2k**) and diphenylphosphanyl-(pyridin-2-ylamino)-acetic acid (**1k**).* A solution of GAH (0.50 g, 5.43 mmol) in diethyl ether (10 mL) was added to a solution of Ph$_2$PH (1.0 g, 5.37 mmol) and 2-aminopyridine (0.50 g, 5.31 mmol) in diethyl ether (15 mL). Precipitation started after few minutes. After stirring overnight the precipitate was separated, washed with a small amount of ether (15 h) and dried under vacuum to give 1.38 g (73%) of **2k**. Anal. Calcd for C$_{19}$H$_{19}$N$_2$O$_3$P (354.34): C, 64.40; H, 5.40; N, 7.91. Found: C, 64.35; H, 5.20; N, 7.83. In [D$_8$]THF solution, ca. 2 h after sample preparation), a mixture of **2k**, **3k** and **1k** was formed, ratio ca. 13:66:17 (by ^{31}P NMR integral. The amount of **1k** increased at the expense of **2k**, after 6 h and during 10 h measuring time to 45:55 (by ^{13}C NMR integration of the PCH signal). **2k**–^{1}H NMR ([D$_8$]THF): δ=5.00 (d, $^1J_{PH}$=1.8 Hz, 1H, PCH), 4.9–5.6 (s br, NH, OH), 6.46–6.52 (m, 2H, 3-H, 5-H), 7.21–7.32 (m, 6H, Ph), 7.36–7.62 (m, 5H, Ph, 4-H), 7.80 (m, 1H, 6-H); 3.26 (MeOH). ^{13}C{^{1}H} NMR and DEPT-135 ([D$_8$]THF): δ=73.41 (d, ^1J=25.4 Hz, PCHO), 110.03 (s, 3-CH), 113.54 (s, 5-CH), 128.58 (d, ^3J=5.9 Hz, *m*-CH$_A$), ca. 128.75 (superimposed d, ^3J=6.7 Hz, *m*-CH$_B$), 129.12 (s, *p*-CH$_A$), 129.21 (s, *p*-CH$_B$), 134.75 (d, ^2J=19.2 Hz, *o*-CH$_A$), 134.96 (d, ^2J=19.2 Hz, *o*-CH$_B$), 139.49 (br, 4-CH), 144.56 (br, 6-CH), 159.55 (br, 2-C$_q$); *i*-C$_q$ and COOH at noise level). ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=5.0.

1k–^{13}C{^{1}H} and DEPT-135 NMR (D$_8$-THF): δ=54.78 (d, ^1J=20.8 Hz, PCHN), 110.15 (d, ^4J=9.3 Hz, 3-CH), 112.33 (s, 5-CH), 128.75 (superimposed d, ^3J=6.7 Hz, *m*-CH$_A$), 128.92 (d, ^3J=6.6 Hz, *m*-CH$_B$), 129.40 (s, *p*-CH$_A$), 129.64 (s, *p*-CH$_B$), 133.74 (d br, ^1J=18.0 Hz, *i*-C$_{qA}$), 134.28 (d, ^2J=19.7 Hz, *o*-CH$_A$), 134.89 (d, ^2J=21.1 Hz, *o*-CH$_B$), 137.06 (d br, ^1J=18.0 Hz, *i*-C$_{qB}$), 137.17 (s, 4-CH), 148.16 (s, 6-CH), 158.77 (d, ^3J=4.0 Hz, 2-C$_q$), 172.78 (d, $^2J\approx$9 Hz, COOH). ^{31}P{^{1}H} NMR ([D$_8$]THF): δ=1.2.

*4.2.12. 4,6-Dimethylpyrimid-2-ylammonium diphenylphosphanyl(hydroxy)acetate (**2l**) and detection of diphenylphosphanyl(4,6-dimethyl-pyrimid-2-ylamino)acetic acid (**1l**).* A solution of Ph$_2$PH (1.0 g, 5.37 mmol) and 4,6-dimethylpyrimidin-2-ylamine (0.66 g, 5.40 mmol) in diethyl ether (20 mL) was added to a solution of GAH (0.50 g, 5.43 mmol) in diethyl ether (10 mL). Precipitation started after ca. 15 h. Stirring was continued for 1 d, the precipitate separated, washed with diethyl ether and dried under vacuum, yielding 1.46 g (74%) **2l**. Anal. Calcd for C$_{20}$H$_{20}$N$_2$O$_3$P (365.37): C, 65.75; H, 5.52; N, 11.50. Found: C, 65.32; H, 5.76; N, 11.50. ^{1}H NMR ([D$_8$]THF): δ=2.16 (s, 6H, 2-Me, 6-Me), 5.04 (d, $^2J_{PH}$=2.6 Hz, 1H, PCHO), 6.22 (s br, 2H, NH$_2$), 6.28 (s, 1H, 5-CH), 6.5–7.1 (extremely broad, 2H, NH/OH), 7.23–7.32, 7.40–7.62 (m, 10H, Ph-H). ^{13}C{^{1}H} and DEPT-135 NMR ([D$_8$]THF): δ=23.30 (s, 2 CH$_3$), 75.13 (d, ^1J=24.9 Hz, PCHO), 109.36 (s, 5-CH), 128.56 (d, ^3J=7.0 Hz, *m*-CH$_A$), 128.70 (d, ^3J=7.1 Hz, *m*-CH$_B$), 129.25 (s, *p*-CH$_A$), 129.28 (s, *p*-CH$_B$), 134.69 (d, ^2J=19.9 Hz, 2 *o*-CH$_A$), 134.80 (d, ^2J=19.5 Hz, 2 *o*-CH$_B$), 136.37 (d, ^1J=17.2 Hz, *i*-C$_{qA}$), 137.42 (d, ^1J=14.8 Hz, *i*-C$_{qB}$), 163.90 (s, 1-C$_q$), 167.88 (s, 4-C$_q$, 6-C$_q$), 175.14 (d, $^1J_{PC}$=10.7 Hz, COOH). ^{31}P{^{1}H}-NMR ([D$_8$]THF): δ=4.3.

In [D$_8$]THF solution minor amounts of **1l**, **3l** and **4l** were formed, (δ^{31}P=2.7, 26.1, −18.0; by P integration 10, 8, 2% after ca. 2 h). The content of **1l** increased to about 20% during the ^{13}C NMR measurement (10 h). **1l**–^{13}C{^{1}H} and DEPT-135 NMR ([D$_8$]THF): δ=23.67 (s, 2 CH$_3$), 54.85 (d, ^1J=25.2 Hz, PCHN), 110.35 (s, 5-CH), 128.78 (d, ^3J=7 Hz, *m*-CH$_A$), 129.03 (d, ^3J=6.7 Hz, *m*-CH$_B$), 129.51 (s, *p*-CH$_{A,B}$), 134.43 (d, ^2J=18 Hz, 2 *o*-CH$_A$), 134.56 (d, ^2J=19.9 Hz, 2 *o*-CH$_B$), 136.40 (d, $^1J\approx$17 Hz, *i*-C$_{qA}$), 137.77 (d, $^1J\approx$17 Hz, *i*-C$_{qB}$), 162.37 (s, 1-C$_q$), 167.63 (s, 4-C$_q$, 6-C$_q$), 172.5 (d, $^1J_{PC}\approx$7 Hz, COOH). Indicative for *meso*/*rac*-**3l** are two PCH proton doublets at δ=5.68 and

5.79 (each $^2J_{PH}$=9 Hz), typically for diphenylphosphonio-bis(glycolates) **3**.[18a]

4.3. Selected reactions of *N*-substituted diphenylphosphanylglycines

*4.3.1. Detection of **5c** and **6c** by air oxidation of **1c**.* A slow stream of oxygen, generated by addition of 30% H_2O_2 on MnO_2, was passed through a drying tube filled with $CaCl_2$ and introduced into a solution of **1c**·MeOH in methanol for 1 h. Removal of the solvent under vacuum and NMR monitoring in $CDCl_3$ displayed formation of a mixture of $Ph_2P(O)CH(NHtBu)COOH$ $tBuNH_3^+$ $Ph_2P(O)CH(OH)COO^-$ (**5c**) and $tBuNH_3^+$ $Ph_2P(O)CH(OH)COO$ (**6c**), identified by conclusive NMR data. **5ce** ^{1}H NMR ($CDCl_3$): δ=1.05 (s, CMe_3), 4.22 (d, $^2J_{PH}$=15.6 Hz, PCHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=27.70 (s, *Me*$_3$C), 54.37 (d, ^3J=9.9 Hz, Me$_3$C), 58.55 (d, ^1J=69.7 Hz, PCHN), 170.08 (s, COOH); aryl-C superimposed). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=30.4. **6c**—^{1}H NMR ($CDCl_3$): δ=1.26 (s, CMe_3), 4.84 (d, $^2J_{PH}$=5.2 Hz, PCHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=28.00 (s, *Me*$_3$C), 51.24 (s, Me$_3$*C*), 71.67 (d, ^1J=79.8 Hz, PCHO), 171.68 (s, COO^-). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=32.0. These values are in good accordance with recently published NMR data of **6c**.[18a]

*4.3.2. tert-Butylamino(diphenylphosphinothioyl)acetic acid (**7c**).* Sulfur (90.5 mg, 2.83 mmol) was added to a solution of **1c**$MeOH (893 mg, 2.57 mmol) in THF (ca. 15 mL). After stirring the mixture at room temperature for 15 h the solvent was removed in vacuum. The residual white foam was treated with diethyl ether to give 0.55 g (62%) of pure **7c**, mp. 106–107 °C (dec). DTG/DTA (15–250 °C, 5 K/min, N_2): Δm117 °C 12.7% ($-CO_2$), max.$_{exoth.}$ 116–117 (st), max.-$_{endoth.}$ 118–120 (st) °C. **7c** is insoluble in D_2O, soluble in methanol, in $CDCl_3$ and in THF. Anal. Calcd for $C_{18}H_{22}NO_2PS$ (347.42): C, 62.23; H, 6.38; N, 4.03. Found: C, 61.91; H, 6.36; N, 3.98%. ^{1}H NMR ($CDCl_3$): δ=1.28 (s, 9H, CMe_3), 4.08 (d, $^2J_{PH}$=10.7 Hz, 1H, CH), 7.35–7.73 (m, 8H, Ph), 8.52 (m, $^3J_{PH}$=13.6 Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=27.2 (*CMe*$_3$), 57.3 (d, ^3J=3.4 Hz, *C*Me$_3$), 57.5 (d, ^1J=39.7 Hz, PCH), 128.4 (d,^3J=13.4 Hz, *m*-CH), 128.6 (d, ^1J=87.5 Hz, *i*-C), 129.0 (d,^3J=13.2 Hz, *m*-CH′), 129.2 (d, ^1J=85.2 Hz, *i*-C′), 132.1 (d, ^2J=11.3 Hz, *o*-CH), 132.5 (d, ^4J=3.1 Hz, *p*-CH), 132.8 (d, ^4J=3.1 Hz, *p*-CH′), 133.0 (d, ^2J=10.9 Hz, *o*-CH′), 164.8 (s, COO^-). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=51.5.

Solutions of **7c** in $CDCl_3$, in [D_8]THF or in CD_3OD underwent slow decarboxylation to **9c** at room temperature (in $CDCl_3$ 67% after 6 d, in [D_8]THF 60% after 3 d and in CD_3OD 40% after 3 d). **9c**—^{1}H NMR ($CDCl_3$): δ=1.11 (s, 9H, CMe_3), 3.53 (d, $^2J_{PH}$=8.7 Hz, 2H, PCH), 7.40–7.70 (m, 6H, Ph), 7.88 (ddd, $^3J_{PH}$=12.9, ^3J=8.1, ^3J=1.5 Hz, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=28.5 (*CMe*$_3$), 51.7 (d, ^3J=13.7 Hz, *C*Me$_3$), 45.6 (d, ^1J=67.7 Hz, PCH_2), 128.5 (d,^3J=12.0 Hz, 4 *m*-CH), 131.58 (d,^2J=10.0 Hz, 4 *o*-CH′), 131.63 (d, ^4J=2.0 Hz, 2 *p*-CH), 131.90 (d, ^1J=80.6 Hz, 2 *i*-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=41.9.

In D_2O/CD_3OD solution immediate deuterolysis took place to give $tBuNH_3^+$ $Ph_2P(S)CH(OH)COO^-$ (**8c**), identified by good accordance of ^{1}H, ^{13}C and ^{31}P NMR data with recently reported values.[18a]

*4.3.3. Diphenylphosphinothioyl(2-pyrid-2-yl-ethylamino)acetic acid (**7g**).* Sulfur (32 mg, 1.0 mmol) was added to **1g**·MeOH (350 mg, 0.88 mmol) in methanol (10 mL). After stirring for 24 h colorless needles were separated, washed with a small amount of MeOH and dried under vacuum to yield 373 mg (98%) of the methanol solvate. Anal. Calcd for $C_{21}H_{21}N_2O_2PS{\cdot}CH_3OH$ (428.48): C 61.67; H 5.88; N 6.54. Found: C 61.62, H 5.82, N 6.55. ^{1}H NMR ([D_8]THF): δ=2.73 (q, ^3J=6.3–6.7 Hz, 2H, $NCCH_2$), 2.75–3.02 (m, 2H, NCH_2), 4.50 (d, $^2J_{PH}$=13.5 Hz, 1H, PCH), 6.94–6.99 (m, 2H, aryl), 7.22–7.38, (m, 6H, aryl), 7.41 (td ^3J=7.7, 7.6, ^4J=1.9 Hz, 1H, H-4), 7.74–7.85 (m, 2H, aryl), 7.88–7.97 (m, 2H, aryl), 8.32 (dd, ^3J=5.4, ^4J=1.9 Hz, 1H, H-6). $^{13}C\{^1H\}$ NMR ([D_8]THF): δ=38.96 (*NCCH*$_2$), 49.76 (s, MeOH), 49.57 (d, ^3J=13.8 Hz, NCH_2), 64.93 (d, ^1J=59.3 Hz, PCH), 121.65 (5-CH), 123.83 (3-CH), 128.49 (d, ^3J=12.4 Hz, *m*-C_A), 128.54 (d, ^3J=12.1 Hz, *m*-C_B), 131.89 (d, ^4J=3.0 Hz, *p*-C_A), 131.93 (d, ^4J=3.2 Hz, *p*-C_B), 132.96 (d, ^2J=10.3 Hz, *o*-C_A), 133.10 (d, ^2J=11.2 Hz, *o*-C_B), 133.60 (d, $^1J \approx$65 Hz, *i*-C_A), 133.94 (d, ^1J=66.2 Hz, *i*-C_B), 136.56 (s, 4-CH), 149.76 (s, 6-CH), 161.01 (s, 2-C_q), 169.93 (d, ^2J=4.8 Hz, COOH). $^{31}P\{^1H\}$ NMR ([D_8]THF): δ=43.9.

In [D_8]THF solution minor amounts of the decarboxylation product **9g** were formed (ca. 25% by integration of PCH_2/PCH proton signals). **9g**—^{1}H NMR ([D_8]THF): δ=3.62 (d, ^2J=6.7 Hz, PCH_2, 25%); other signals superimposed. $^{13}C\{^1H\}$ NMR ([D_8]THF): δ=37.88 (s, $NCCH_2$), 51.18 (d, ^3J=13.4 Hz, NCH_2), 52.64 (d, ^1J=64.1 Hz, NCH_2), 121.70 (5-CH), 123.76 (3-CH), 129.00 (d, ^3J=11.9 Hz, 4 *m*-CH), 131.61 (d, ^4J=3.6 Hz, 2 *p*-CH), 132.31 (d, ^3J=10.2 Hz, 4 *o*-CH), 136.65 (4-CH); *i*-C_q, 6-CH and 2-C_q superimposed. $^{31}P\{^1H\}$ NMR ([D_8]THF): δ=38.7 (rel intensity 15%).

*4.3.4. [{$Ph_2P(BH_3)CH(NHtBu)COO$}$_3B^-$($OOC(tBuNH_2^+)CHP(BH_3)Ph_2$] (**10c**).* A solution of $H_3B{\cdot}SMe_2$ in THF (1.5 mL, 1.5 mmol, 2.6 equiv) was added slowly at 0 °C to a freshly prepared solution of crude **2c** (δ^{31}P=8.1; 200 mg, 0.58 mmol) in THF (10 mL), accompanied to strong evolution of hydrogen. Then, the mixture was allowed to warm to room temperature and stirred overnight. Most of the solvent was removed under vacuum and the residue filtered and washed with hexane to give 190 mg (96%) white powder, mp. 116–118 °C. Calcd for $C_{72}H_{97}B_5N_4O_8P_4$ (1324.51): C 65.29, H 7.38, N 4.23. Found: C 63.23 (incomplete combustion), H 7.73, N 4.35%. ^{1}H NMR ($CDCl_3$): δ=0.5–3.5 (br m, ca. 12H, BH_3), 1.33 (s, 36H, CMe_3), 4.33 (dd, $^2J_{PH}$=8.2, J=1.2 Hz, 4H, PCH), 5.61 (d, $^3J_{PH}$=10.5 Hz, 4H, NH), 7.38–7.55, 7.58–7.74, 8.19–8.28 (m, Ph, NH^+). ^{13}C NMR ($CDCl_3$): δ=25.42 (*CMe*$_3$), 56.58 (d, ^1J=24.4 Hz, PCHN), 60.40 (d, ^3J=3.6 Hz, *C*Me$_3$), 123.61 (d, ^1J=55.9 Hz, *i*-C_q), 125.28 (^1J=63.2 Hz, *i*-C_q′), 128.74 (^3J=11.3 Hz, *m*-CH), 129.50 (^3J=11.0 Hz, *m*-CH′), 132.62 (^4J=2.6 Hz, *p*-CH), 132.71 (^4J=2.7 Hz, *p*-CH′), 133.46 (^2J=10.0 Hz, *o*-CH), 133.84 (^2J=10.9 Hz, *o*-CH′), 169.23 (^2J=4.2 Hz, COO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=25.8 (br d appearance of overlayered multiplets with ^{31}P—^{10}B- and ^{31}P—^{11}B-coupling). ^{11}B NMR ($CDCl_3$): δ=−0.7 (vbr, BO_4), −40.5 (br, H_3B—P).

*4.3.5. Detection of (tert-butylamino-diphenylphosphanylacetic acid κ^1-P)pentacarbonyltungsten (**11c**).* Solid **1c**·MeOH (170 mg, 0.49 mmol) was added to a solution of $W(CO)_5THF$, prepared from $W(CO)_6$ (380 mg, 0.85 mmol) in THF (60 mL) at 20 °C by UV irradiation with a cooled mercury-immersion lamp (evolution of 19 mL, 0.85 mmol of CO). After stirring for 6 h at room temperature the major part of the solvent was evaporated in vacuum. CH_2Cl_2 (15 mL) was added to the residual 3–5 mL, the mixture filtered and the solution stored for 3 d at −24 °C. The pale yellow crystals (251 mg) formed were separated, washed with CH_2Cl_2 (5 mL) and dried in vacuum. The NMR spectra indicated **11c**, contaminated by $(Ph_2PH)W(CO)_5$ and a trace of η^1-*P*-(Ph_2PCH_2NHtBu)$W(CO)_5$ (^{31}P NMR signal heights 65:27:8%). **11c**—^{1}H NMR ($CDCl_3$): δ=0.99 (s, 9H, 3 Me), 4.27 (d, $^2J_{PH}$=10.0 Hz, 1H, PCH), 7.36–7.68 (m, 10H, 2 Ph). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ=29.07 (*CMe*$_3$), 52.68 (d, $^3J_{PC}$=10.6 Hz, *C*Me$_3$), 59.70 (d, $^1J_{PC}$=26.1 Hz, PCH), 127.92 (d, ^3J=9.2 Hz, 2 *m*-CH_A), 128.10 (d, $^3J_{PC}$=9.4 Hz, *m*-CH_B), 130.04 (*p*-CH_A), 130.57 (*p*-CH_B), 132.81 (d, $^2J_{PC}$=9.6 Hz, 2 *o*-CH_A), 133.12 (d, $^1J_{PC}$=37.0 Hz, *i*-C_{qA}), 134.04 (d, $^2J_{PC}$=11.0 Hz, 2 *o*-CH_B), 135.79 (d, $^1J_{PC}$=37.4 Hz, *i*-C_{qB}), 175.27 (d, ^2J=9.2, COO^-), 197.02 (d satl, $^2J_{PC}$=6.7, $^1J_{PW}$=127.6 Hz, 4 *cis*-CO), 199.40 (d satl, $^2J_{PC}$=23.9, $^1J_{PW}$=143.3 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=26.7 (satl, $^1J_{PW}$=248 Hz).

(Ph_2PH-κ^1P)$W(CO)_5$—$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=−12.73 (satl, $^1J_{PW}$=230 Hz); ^{1}H NMR: PH and phenyl signals superimposed; ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ=129.10 (d, ^3J=9.5 Hz, 4 *m*-CH), 132.32 (d, $^2J_{PC}$=11.9 Hz, 4 *o*-CH), 132.32 (d, $^1J_{PC}$=43.8 Hz, 2 *i*-C_q); *p*-CH superimposed. (Ph_2PCH_2NHtBu-κ^1P)$W(CO)_5$—$^{31}P\{^1H\}$ NMR

($CDCl_3$): δ=11.15 (satl, $^1J_{PW}$=241.5 Hz). ^{1}H NMR ($CDCl_3$): δ=1.01 (CH_3), 3.57 (d, $^2J_{PH}$=3.5 Hz, PCH_2), phenyl signals superimposed. ^{13}C NMR ($CDCl_3$): δ=28.53 (CMe_3), 46.43 (d, ^1J=37.1 Hz, PCH_2N), 51.41 (^3J=10.6 Hz, CMe_3), 128.65 (d, ^3J=9.3 Hz, 4 *m*-CH), 130.3 (2 *p*-CH), 132.22 (d, ^2J=10.6 Hz, 4 *o*-CH), 134.63 (d, ^1J=39.5 Hz, 2 *i*-C_q).

*4.3.6. [Diphenylphosphanyl(quinolin-8-ylamino)acetic acid κ^1-P] pentacarbonyltungsten (**11i**).* Solid **1i**·MeOH (431 mg, 1.03 mmol) was added to a solution of $W(CO)_5$(THF), prepared from $W(CO)_6$ (363 mg, 1.03 mmol) in THF (60 mL) at 20 °C, and after 6 h at room temperature the product worked up as described for **11c** to give 352 mg (48%) of **11i**. Anal. Calcd for $C_{28}H_{19}N_2O_7PW$ (710.04): C 47.35; H 2.70; N 3.94. Found: C 47.35, H 2.55, N 3.84. ^{1}H NMR ($CDCl_3$): δ=5.19 (unresolved t, $^2J_{PH}+^3J$=17.3 Hz, 1H, PCH), 6.78 (d, ^3J=7.2 Hz, 1H, H-7), 6.90 (unresolved *t*, $J+J' \approx 12$ Hz, 1H, NH), 7.19 (d, ^3J=8.0 Hz, 1H, H-5), 7.30–7.50 (m, 8H, H-3, H-6, Ph), 7.55–7.75 (2m, 4H, Ph), 8.05 (d, ^3J=7.9 Hz, 1H, H-4), 8.64 (br, 1H, H-2). ^{13}C{^{1}H} and DEPT-135 NMR ($CDCl_3$): δ=58.75 (d, ^1J=16.6 Hz, PCHN), 106.68 (s, 7-CH), 117.07 (s, 5-CH), 121.73 (s, 3-CH), 127.27 (s, 6-CH), 128.52 (s, 10-C_q′), 128.70 (d, ^3J=9.6 Hz, 2 *m*-CH_A), 128.72 (d, ^3J=9.2 Hz, 2 *m*-CH_B), 130.91 (s, *p*-CH_A), 130.97 (s, *p*-CH_B), 132.78 (d, ^1J=36.9 Hz, 2 *i*-C_q), 132.70 (d, ^2J=11.9 Hz, 2 *o*-CH_A), 132.94 (d, ^2J=11.7 Hz, 2 *o*-CH_B), 135.87 (s, 4-CH), 138.45 (s, 9-C_q), 142.40 (d, ^3J=6.3 Hz, 8-C_q), 147.61 (s, 2-CH), 172.43 (d, ^2J=6.3 Hz, COOH), 196.29 (d, ^2J=6.8 Hz, 4 *cis*-CO), 198.76 (d, ^2J=24.2 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ=28.7 (satl., $^1J_{PW}$=249.7 Hz).

4.4. Ethylene oligomerization

A freshly prepared solution or suspension of **1** (ca. 0.1 mmol) in THF (10 mL) or toluene (10 mL) was added at 0 °C to a freshly prepared solution of $Ni(COD)_2$ (ca. 0.1 mmol) in THF. For the screening in THF/water (15:5 mL) and in THF/1-hexene, respectively, each the THF amount was used to prepare the pre-catalyst mixture, followed by addition of the water or 1-hexene. After stirring for 10 min at 0–5 °C and 15–30 min at room temperature the mixtures were transferred via a Teflon tube into the stainless steel autoclave, equipped with a powerful magnetic stirrer, safety diaphragm, manometer and sensor for pressure registration over the reaction time. The weighted autoclave was pressurized with ethylene (30–50 bar, see Table 1), the tightness and mass of ethylene were checked and the autoclave heated in a silicon oil bath to 100 °C for 15–17 h. After cooling to 0–10 °C unconverted ethylene was released through a cooling trap to condense butenes and vapors of lower alkenes. The content was transferred into a flask and volatiles were flash-distilled at 80 °C/10^{-1} Torr into a cooling trap (−96 °C). Solid residue was treated for 1 d with MeOH/conc. hydrochloric acid (1:1), washed repeatedly with methanol and dried under vacuum. The solids were characterized by ^{1}H NMR measurement at 100 °C in C_6D_5Br solution (acquisition time 4.9–5.4 s, delay 1.0 s, reference *p*-CH of solvent δ=7.23) after swelling for 1 d at 100 °C, by melting ranges and in part by density of tablets, pressed at 70 kbar, determined using the sinking method in EtOH/water (detergents). The flash distillates were analyzed by GC (HP 5890), column 30 m HP-5 (5% crosslinked PhMe silicon), 20 min 30 °C, 20°/min, 10 min 250 °C, FI detector. The results are compiled in Table 1.

4.5. Crystal structure analyses

X-ray diffraction data for **1b**·1.43MeOH and **1h**·MeOH were recorded on a Bruker/Nonius Apex X8-CCD diffractometer at 173 K. All measurements were performed using monochromated MoK_α radiation (λ=0.71073 Å). The data were corrected for absorption effects using the SADABS procedure.[39] The structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 (SHELXL-97).[40] All non-hydrogen atoms were refined anisotropically. H-atoms were calculated assuming idealized geometries and refined using riding models. Crystallographic data are given in Table 2 and selected bond lengths and angles in Figs. 2 and 3.

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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.2015.05.101.

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