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α-Phosphanyl Amino Acids: Synthesis, Structure and Reactivity of *N*-Aryl-α-phosphanylglycines

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Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 80th birthday

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The novel *N*-aryl-α-phosphanylglycines **1a**–**d** have been easily prepared by one-pot three-component reactions of diphenylphosphane, primary arylamines and glyoxylic acid hydrate in diethyl ether. The reactions proceed via intermediate arylammonium (diphenylphosphanyl)glycolates **2** and stop at this stage in the case of N-secondary anilines, for example, the stable *N*-methylanilinium phosphanylglycolate **3**. The conversion of **2** into **1** is an equilibrium, as demonstrated by the reversible hydrolysis of **1b** to **2b** in [D_8]THF containing varying amounts of water. The solid α-phosphanyl amino acids are stable, but in THF or DMSO solution they suffer from slow decarboxylation, which becomes rapid on heating at about 80 °C, yielding N-secondary phosphanylmethylanilines **4**. Solutions of **1** in the polar protic solvent methanol are stable over long periods, but show rapid proton/deuterium exchange even of the α-CH proton in deuteriomethanol and thus increased CH acidity compared with normal α-amino acids. This and the sensitivity to hydrolysis hint at an acetal-like character and partial protonation even at the phosphorus atom. Oxidation of the *N*-aryl derivatives **1b**,**c** by aqueous H_2O_2 proceeds more rapidly than hydrolysis and provides the first examples of phosphinoylglycines **5**. Oxidation by sulfur is rapid even at room temperature in methanol, giving the thiophosphinoylglycines **6**. The coordination properties of **1** at the phosphanyl group are characterized by the reaction of **1b** with [$M^{VI}(CO)_5$(THF)] (M^{VI} = Cr, Mo, W) and the coordination chemical shifts in the NMR spectra and ν_{CO} shifts in the IR spectra of the resulting [(**1b**)$M^{VI}(CO)_5$] complexes **7b**–**9b**. The structures of the new compounds were elucidated by crystal structure analysis of **1b** and **6b** and the solution NMR spectroscopic data of all the compounds. Screening for the nickel-catalysed oligomerization of ethylene showed the formation of active catalysts from **1** and Ni(cod)$_2$.

Introduction

Synthetic amino acids are of interest in various fields of chemistry, biochemistry and pharmacy.[1] The first representatives with a phosphanyl group were obtained by condensation of natural amino acids with secondary phosphanes and formaldehyde, usually forming bis(phosphanylmethyl) amino acids, and studied with respect to their use as ligands in rhodium-catalysed hydrogenation reactions and in complexes for radio-diagnostics.[2] The use of primary phosphanes extended the range of *N*-phosphanylmethyl amino acids to various P,N-heterocyclic types.[3] Instead of PH compounds, the formaldehyde adducts thereof can also be used.[4] Since 1996 several amino acids with a phosphanyl group on the phenyl ring of phenylglycine and phenylalanine[5,6] or in the β position ("phosphinoserines"[7,8] and 4-phosphanylprolines[9,10]) have been reported, as have their oligopeptides and catalytic screenings.[11] An α-phosphanyl dialkylamino acid ester, iPr$_2$PCH(NEt$_2$)CO-OMe, has been obtained from chlorodiisopropylphosphane and the sodium enolate of *N*,*N*-diethylglycine methyl ester,[12] but we have been the first to communicate on acyclic α-phosphanyl amino acids, *N*-alkyl-phosphanylglycines.[13] These compounds proved highly sensitive to hydrolysis, exchanged the alkylamino group for a hydroxy group prior to oxidation when treated with aqueous hydrogen peroxide and well-defined transition-metal complexes have not yet been found. The incorporation of *P*-alkyl instead of *P*-phenyl groups led to an increase in the sensitivity of *N*-alkyl-α-phosphanylglycines. To obtain more stable α-phosphanyl amino acids we systematically varied the nitrogen

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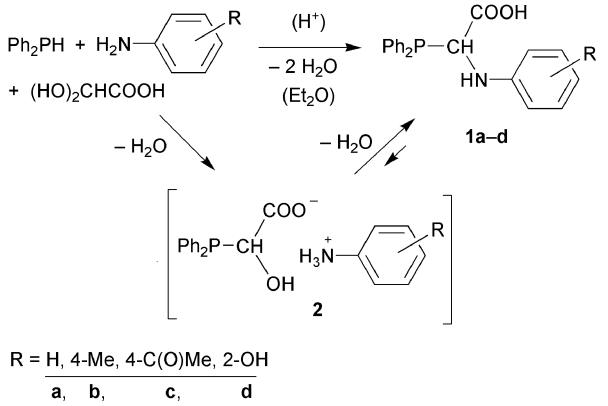
substituents of the (diphenylphosphanyl)glycines and report here on the novel *N*-aryl derivatives **1**, their synthesis, structure and properties, and the first examples of their transition-metal complexes and their use in homogeneous catalysis.

Results and Discussion

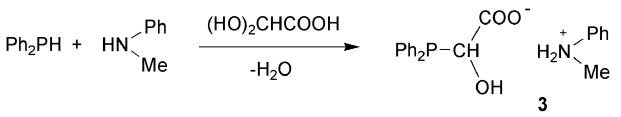
Synthesis of *N*-Aryl-α-(diphenylphosphanyl)glycines

Whereas most of the previously reported *C*-phosphanyl-substituted amino acids were obtained by substitution reactions, replacing a halide or tosylate group of protected amino acids by phosphide, we envisaged the synthesis of the title compounds **1** employing a three-component condensation reaction. For pentavalent P–H compounds of the types $HP(O)R_2$ and $H_2P(O)R$, three-component condensation reactions with amines and aldehydes or ketones are well known as Kabachnik–Fields reactions.[14,15] For trivalent PH compounds such condensation reactions have been reported only for formaldehyde.[3a,16–19] Examples of analogous reactions of aldehydes and ketones could not be found in an extended search although various *C*-substituted α-phosphanyl-alkylamines are available by the addition of phosphanes to Schiff bases.[16,17] Only two-component condensation reactions of ω-phosphanyl-alkylamines or *o*-phosphanylanilines with aldehydes or ketones are known to provide P–C–N heterocycles,[20] which are hydrolytically more stable than acyclic P^{III}–C–N compounds. Usually heating with azeotropic removal of water is required. In related studies on arsenic heterocycles,[21] the condensation of 2-(arsinoalkyl)amines with pyruvic acid took place much more readily than with aldehydes or ketones and furnished the heterocyclic arsanyl amino acids in a strongly exothermic reaction in high yield without the need of further heating. Therefore, in our present search for acyclic α-phosphanyl amino acids, we supposed that the activation of the keto function by the electron-withdrawing COOH group might allow a more facile condensation and thus also three-component reactions with trivalent PH compounds and NH amines, as known for formaldehyde. This assumption proved incorrect for pyruvic acid but successful for the more reactive glyoxylic acid in the case of sterically unhindered and sufficiently basic primary amines.

The reaction according to Scheme 1 proceeds at room temperature simply by adding an ethereal solution of glyoxylic acid monohydrate to a solution of the aromatic amine and diphenylphosphane in diethyl ether and stirring the mixture for some hours. In addition to the phenyl and *p*-tolyl derivatives (**1a** and **1b**), functionally substituted derivatives **1c** and **1d** were also prepared, which demonstrates that the scope of the reaction is sufficiently wide to allow electron-withdrawing or -donating functional groups in the arylamine. Further intramolecular condensation of the COOH and the *o*-hydroxy group of **1d**, with the formation of a six-membered lactol ring, was not observed under these reaction conditions. In contrast to the usually strongly preferred bis-phosphanylmethylation of primary amines with secondary phosphanes and formaldehyde,[2,4,17] only *N*-monosubstitution takes place in the reaction with glyoxylic acid hydrate. This resembles the behaviour of zwitterionic α-amino acids such as alanine under mild conditions[2] and is thus attributed to the presence of the COOH group. Monitoring of the formation of **1b** by ^{31}P and ^{1}H NMR spectroscopy ([D_8]THF) provided evidence for a stepwise reaction. A precipitate formed a few minutes after mixing the ethereal solution of *p*-toluidine and diphenylphosphane with the solution of glyoxylic acid monohydrate; its NMR spectra displayed considerable amounts of *N*-tolylammonium (diphenylphosphanyl)glycolate (**2b**) in addition to the main product **1b** and minor amounts of residual Ph_2PH and an unidentified compound (δ = –5.5 ppm). Glycolate **2b** was indicated by the sharp PC*H* doublet at δ = 4.95 ppm [^2J(PH) = 2.4 Hz] downfield from the PC*H* signal of **1b** (integral ratio ca. 36:64) and by the typical phosphorus resonance of **2b** at δ = 6.4 ppm. These two typical signals are almost identical to those observed in the fully characterized and stable *N*-methylanilinium phosphanylglycolate **3b** formed in the reaction of diphenylphosphane and *N*-methylaniline with glyoxylic acid hydrate (Scheme 2). The route via **2** distinguishes our reaction from the modified Mannich mechanism, discussed for the reactions of phosphanes and NH amines with formaldehyde;[2,3,17] the latter reacts with primary or secondary amines easily to form imines or immonium cations, which add the PH component. We assume that the alternative mechanism is associated with the COOH group, protonating the amine and intramolecularly a hydroxy group of the adjacent $CH(OH)_2$ moiety. After the cleavage of water the addition of phosphane is favoured over the competing additions of water (back reaction) or of unprotonated amine. For the second step, the replacement of the second OH by the amino group, a similar course is expected. The lower rate is attributed to the presence of only one OH group and steric hindrance by the diphenylphosphanyl group. The reaction is driven by the slightly higher stability of **1b**·H_2O compared with **2b**, experimentally shown by the hydrolysis equilibrium in favour of **1b** (see below).

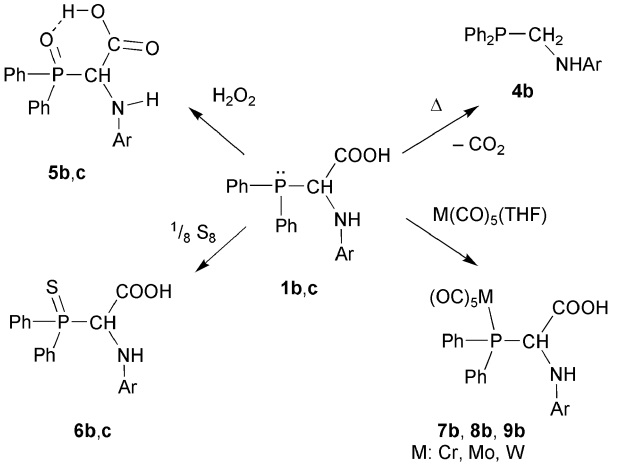


Scheme 1. Three-component synthesis of *N*-aryl-α-(diphenylphosphanyl)glycines **1a**–**d** and the hydrolytic equilibrium between **1** and **2**.



Scheme 2. Formation of (diphenylphosphanyl)glycolate **3**.

The failure of the conversion of **3** to the corresponding *N*-disubstituted α-(diphenylphosphanyl)glycine may be due to steric hindrance or to a lower thermodynamic stability, for example, associated with solvation effects. Harsher reaction conditions in the three-component condensation with glyoxylic acid, that is, heating with azeotropic removal of water, resulted in mixtures. The reason may be the manifold condensation reactions of glyoxylic acid hydrate at an elevated temperature[22] and the sensitivity of phosphanylglycines to thermal decomposition.



Scheme 3. Reactions of *N*-aryl(phosphanyl)glycines **1b**,**c** [Ar: *p*-$CH_3C_6H_4$, *p*-$C(O)CH_3C_6H_4$].

Reactivity

Solid *N*-aryl(diphenylphosphanyl)glycines **1a**–**d** are stable if stored at ambient temperature under an inert atmosphere. However, like (diphenylphosphanyl)acetic acid,[23] they undergo decarboxylation on heating. At 95 °C the reaction is complete within 2 h, in THF at reflux within 4–5 h. Monitoring of the process by NMR reveals mainly **4b** and minor amounts of $(Ph_2PCH_2)_2NpTol$[24] (Scheme 3). The phosphanylglycines **1a**–**d** are slowly attacked by atmospheric oxygen in the crystalline state, but rapidly in solution, resulting in phosphane oxides **5**, detectable by NMR, along with small amounts of $Ph_2P(O)PPh_2$[25] and other byproducts. Sulfur likewise oxidizes phosphanylglycines at room temperature to the corresponding phosphane sulfides, demonstrated on the preparative scale by the synthesis of **6b** and **6c**. For synthetic access to phosphinoylglycines **5**, the oxidation of **1** by excess aqueous hydrogen peroxide (30%) is more suitable than air oxidation and gives pure products. Examples are the conversion of **1b** and **1c** to **5b** and **5c**, respectively. This shows that the *N*-aryl-α-(diphenylphosphanyl)glycines are markedly less sensitive to hydrolysis than *N*-alkyl-α-(diphenylphosphanyl)glycines,[13] which form alkylammonium (diphenylphosphinoyl)glycolates when treated with aqueous H_2O_2.

To quantify the sensitivity of *N*-aryl(phosphanyl)glycines towards moisture, solutions of **1b** in [D_8]THF containing excess water were studied by NMR spectroscopy. The trace phosphorus signal of the hydrolysis product **2b** reversibly increased with temperature. Increased concentrations of water led to increased ratios of **2b**:**1b**. These findings indicate a temperature- and concentration-dependent hydrolytic equilibrium of **2b** and **1b** in THF (at 25 °C [**2b**]/{[**1b**]([H_2O]–[**2b**])} = 8×10^{-4} mmol^{-1} based on the ^{1}H integration of *p*-Me signals) and that **1b**·H_2O is more stable than **2b**. In CD_3OD solution the hydrolysis of **1b** is also minor. The hydrolytic equilibrium is accompanied even at room temperature by slow decomposition reactions leading irreversibly to the aforementioned decarboxylation product **4b** (preferred in [D_8]THF) and to small amounts of Ph_2PH (preferred in CD_3OD). The much lower extent of hydrolysis in the *N*-aryl- compared with the *N*-alkyl-α-(diphenylphosphanyl)glycines is attributed to the much lower basicity of the arylamino groups and hydrolysis by elimination of amines from the *N*-protonated form of **1**. The detection of Ph_2PH shows that even the very weakly basic diphenylphosphanyl group is slowly cleaved by P-protonation. Thus, it can be assumed that the reduced hydrolytic stability of phosphanylglycines compared with normal α-amino acids is caused by the P,N-acetal nature of **1** and destabilizing protonation by the adjacent COOH group. Hence, one might expect greater stability for coordination compounds of the α-phosphanyl amino acids with the electron lone-pair at phosphorus blocked by less destabilizing electrophiles than the proton.

Attempts to stabilize **1a**–**d** as BH_3 adducts by reaction with Me_2S–BH_3 in THF in a molar ratio of 1:1 to 1:3 led to mixtures of phosphanylboranes with downfield shifted and broad phosphorus resonances, but failed to give defined pure compounds. The wide spectrum of transition-metal electrophiles should, however, offer the possibility of stabilizing the ligands in their complexes and, in addition, might reveal potential applications of the sensitive but easily accessible phosphorus ligands.

The η^1-P coordination properties of *N*-aryl-α-phosphanylglycines were studied by reactions of **1b** with [$M(CO)_5$-(THF)] in THF (M = Cr, Mo, W). If solid **1b** is added to a solution of [$M(CO)_5$(THF)] in THF, the complexes **7b**–**9b** are formed in a pure state. Generation of the complexes directly at the surface of **1b** prevented side-reactions of **1b** in solution. If solutions of **1b** in [D_8]THF are combined with [$W(CO)_5$(THF)], the formation of **9b** can be detected by ^{31}P NMR along with substantial amounts of [(Ph_2PH)-$W(CO)_5$][28] and a compound tentatively assigned as [$Ph_2P_A(O)P_B(Ph_2)W(CO)_5$] on the basis of characteristic $^1J_{PP}$ and $^1J_{PW}$ couplings. The compounds **7b**, **8b** and **9b** are the first examples of defined transition-metal complexes of (diphenylphosphanyl)glycines. The coordination by the phosphorus markedly changes the solubility properties. In

contrast to **1b** and phosphanylglycines in general, the η^1-*P*-coordinated group 6 metal pentacarbonyl complexes **7b**–**9b** are all soluble in $CDCl_3$. In the NMR spectra the coordinated ^{31}P nuclei display strong downfield coordination shifts, decreasing in the order Cr > Mo > W [$\Delta\delta^{31}(P_{complex-ligand})$ = 64.8, 46.6, 27.2 ppm]; the same trend is shown by the ^{13}C nuclei of the carbonyl groups. The $\Delta\delta(^{31}P)$ values lie in the upper range of those typical of [(diphenylalkylphosphane)$M^{VI}(CO)_5$] complexes.[26] The chemical shifts of the α-C atoms, P*C*H and *i*-*C*(Ph) are little affected, likewise the $^1J_{PC}$ coupling constants of the sp^3-hybridized α-C atom, whereas the $^1J_{PC}$ value of the sp^2-hybridized *i*-C is increased from 16–18 to 32–40 Hz. The one-bond ^{31}P–^{183}W coupling constant in **9b** (249 Hz) and the bathochromic shifts of the carbonyl stretching frequencies in **7b**–**9b** (A_1 mode: 2064, 2073, 2071 cm^{-1}; E mode: 1940, 1951, 1938 cm^{-1}), both indicative of the donor ability of the phosphane ligands in [$R_3PW(CO)_5$] complexes,[26,27] display similar values to those of conventional [(diphenylalkyphosphane)$M(CO)_5$] complexes.

Although the electron lone-pair at the phosphorus of **1b** is blocked by coordination to soft $M(CO)_5$ fragments and the coordination properties seem to parallel those of stable [(diphenylalkylphosphane)$M(CO)_5$] complexes, solutions of **7b**–**9b** in [D_8]THF decompose slowly if stored for some days. Even the somewhat more stable tungsten complex **9b** decomposes completely when subjected to column chromatography on silica gel and elution with variable amounts of *n*-hexane/dichloromethane. Detection of [$(Ph_2PH)W(CO)_5$] by characteristic ^{31}P NMR spectroscopy gives evidence of proton-mediated P–C bond cleavage.

Although so far no complexes other than the above-mentioned η^1-*P*–transition metal(0) systems could be isolated as defined compounds, there are hints of the formation of nickel complexes. Solutions of **1b** or **1c** and $Ni(cod)_2$ in THF form catalysts with high activity in the oligomerization of ethylene, yielding waxy low-molecular-weight polymers and smaller amounts of flash-distillable oligomers (C_4–C_{12}, mainly C_6 and C_8), both with high selectivity for linear chains with vinyl and methyl end groups (Table 1). Other olefins, for example, 1-hexene, are neither converted into oligomers nor incorporated into the growing ethylene oligomer chain. If 1-hexene is used as the solvent then the chain growth is slow because of competing interactions of the catalyst with this olefin, but it is not inserted into the ethylene oligomer chain. Catalysts formed in situ from (diphenylphosphanyl)acetic acid and $Ni(cod)_2$ or $NiCl_2$ and $NaBH_4$ show the same selectivity.[29] Closer investigation of these industrially important catalysts, applied in the Shell Higher Olefin Process,[30] showed that organo- or hydrido-

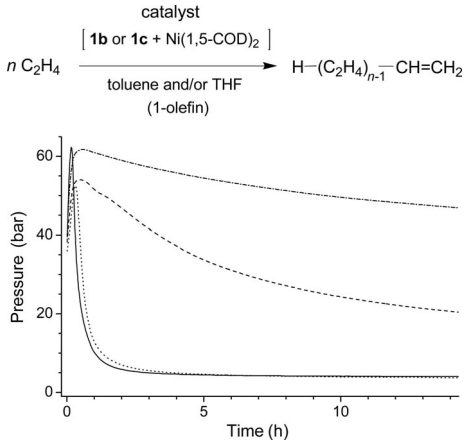


Figure 1. Pressure–time plots for the oligomerization of ethylene catalysed by (a) **1c/Ni** in THF (solid line), (b) **1b/Ni** in THF/1-hexene (50:50 vol.-%; dotted line), (c) **1b/Ni** in 1-hexene (dashed line), (d) **1c/Ni** in 1-hexene (dash-dot line).

Table 1. Oligomerization of ethylene by catalysts generated in situ from **1b** or **1c** and $Ni(cod)_2$.

Entry	C_2H_4 [g, mmol]; solvent [mL]	Ligand, Ni [mmol]; p_{start} [bar], *T* [°C], *t* [h]	Conversion [g, %]; TON [mol/mol], TOF [mol/mol h]	PE wax [g];[a] m.p. [°C], ρ [g/cm^3]	^1H NMR:[b] *M* [g/mol]	Vin/internal Olefin	Me/C=C, Me/1000
1	10.8, 385; toluene 10, THF 10	**1b**, 0.1, 0.1; 40, 100, 15	10.6, 98; 3780, n.d.	8.0; 108.6, 0.88	780	76:24	1.6, 29
2	12.6, 449; THF 20	**1b**, 0.09, 0.09; 40, 100, 15	8.2, 65; 2920, n.d.	5.2; 111.0, 0.92	700	88:12	1.3, 25
3	11.2, 399; toluene 20	**1c**, 0.1, 0.1; 40, 100, 16	10.8, 96; 3850, n.d.	5.4; 100, 0.91	715	78:22	1.6, 32
4	13.4, 477; THF 20	**1c**, 0.1, 0.1; 40, 100, 16	13.2, 98; 4700, 13000	10.5.[c] 99–101, 0.91	780	77:23	1.5, 27
5	11.6, 413; THF 10; 1-hexene 10	**1b**, 0.1, 0.1; 40, 100, 16.8	11.4, 98; 4060, 6200	8.7; 91, 0.89	510	70:30	1.8, 48
6	10.2, 364; 1-hexene 20	**1b**, 0.1, 0. 1; 40, 100, 16	7.0, 69; 2500, 300	4.8; 127–129, 0.90	1600	80:20	2.4, 21
7	10.1, 360; 1-hexene 11	**1c**, 0.1, 0.1; 40, 100, 16	3.5, 35; 1250, 100	3.5; 101, 0.90	1086	72:28	2.3, 29

[a] Solvent and lower α-olefins were separated by flash distillation; for purification of the remaining wax, see the Exp. Sect. [b] NMR spectra were measured after swelling (24 h, 100 °C) in C_6D_5Br at 100 °C. [c] ^{13}C NMR spectrum measured in the presence of [$Cr(acac)_3$] (AQ 1.5 s, DE 6.0 s). n.d.: not determined.

nickel(II) (diphenylphosphanyl)acetate complexes are formed and that the catalyst is stabilized by the $\widehat{PO}^-$ chelate backbone.[31] Other types of $\widehat{PO}^-$ nickel chelates, for example, phosphanylbenzoate, -enolate or -phenolate ligands, display the same principal behaviour and selectivity,[32] whereas $\widehat{PN}$ nickel chelate catalysts[33] need MAO or other organo-aluminium compounds to form ethylene oligomerization catalysts. Therefore it can be assumed that the catalysts generated from **1b** or **1c** and $Ni(cod)_2$ are also stabilized by a $\widehat{PO}^-$ chelate backbone and that exploration of the coordination behaviour of the novel α-phosphanyl amino acid ligands will reveal further feasible coordination modes (Figure 1).

Crystal Structures

Detailed structural information on the new *N*-arylglycine phosphorus compounds has been provided by single-crystal X-ray diffraction analyses of **1b** (Figure 2) and **6b** (Figure 3), both grown from methanol. Compound **1b** crystallizes solvent-free, **6b** as a methanol monosolvate. In contrast to the zwitterionic *N*-alkyl(diphenylphosphanyl)glycines,[13] the less N-basic arylamino derivatives **1b** and **6b** display non-dissociated carboxylic acid groups. In **1b** these pack to form the usual inversion-symmetric dimers with O(2)···O(1) 2.6243(12) Å, angle 176.1(19)° (see the Supporting Information), whereas the amino group is not involved in hydrogen bonds. The dimers are connected by additional weak C–H···O interactions: C(16)–H(16)··O(1) (H···O 2.60 Å, angle 131°) and C(22)–H(22)···O(2) (H···O 2.62 Å, angle 141°]. In **6b** the classic hydrogen-bonding is mediated by methanol molecules [C(O)O(2)–H(02)···O(99)(Me)–H(03)···O(1)C(OH): O(2)···O(99) 2.5603(14), O(99)···O(1) 2.7453(15) Å, angles 175(2), 163(2)°] and the dimers extend in a broad ribbon structure parallel to the *z* axis (Figure 4) through much longer N–H(01)···O(2) interactions [N···O 3.2560(16) Å, angle 148(2)°]. In **1b** and **6b** the bond lengths and angles have normal values. The nitrogen atom is sp^2-hybridized [C(11)–N–C(1) 118.71(10), 119.85(11)°], indicative of π interactions with the *N*-tolyl π system. The conformation around the P–C(1) axis is essentially staggered with dihedral angles C(31)–P–C(1)–N of 94.60(8) and 63.49(10)° and C(21)–P–C(1)–N of –160.59(8) and 175.76(8)°.

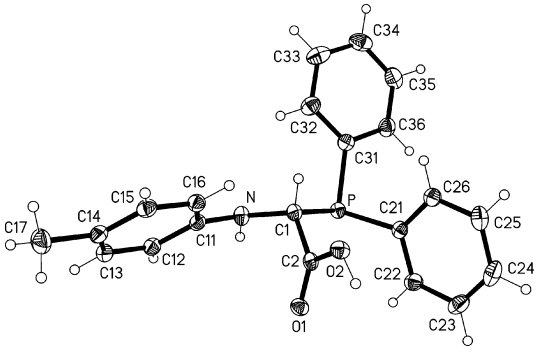


Figure 2. Molecular structure of **1b** in the crystal (ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: P–C(1) 1.8946(12), P–C(21) 1.8325(12), P–C(31) 1.8341(12), C(1)–C(2) 1.5197(16), C(1)–N 1.4521(15), N–C(11) 1.4109(15); C(21)–P–C(31) 102.51(5), C(21)–P–C(1) 99.12(5), C(31)–P–C(1) 101.28(5), N–C(1)–P 106.94(8), C(2)–C(1)–P 107.48(8), N–C(1)–C(2) 113.32(9).

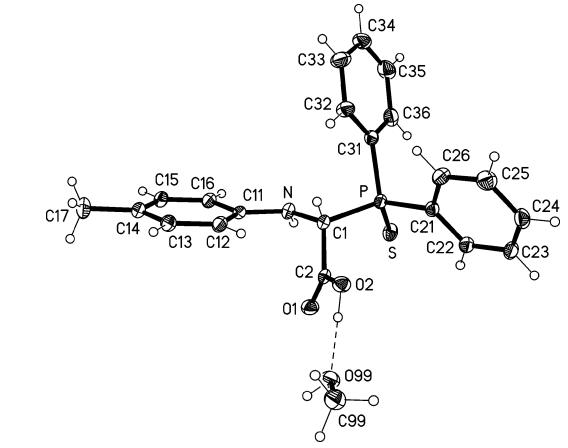


Figure 3. Molecular structure of **6b** in the crystal (methanol solvate; ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: P–C(1) 1.8588(13), P–C(21) 1.8188(14), P–C(31) 1.8194(14), C(1)–C(2) 1.5331(18), C(1)–N 1.4367(17), N–C(11) 1.4116(17); C(21)–P–C(31) 105.70(6), C(21)–P–C(1) 110.18(6), C(31)–P–C(1) 102.76(6), N–C(1)–P 105.00(9), C(2)–C(1)–P 113.61(9), N–C(1)–C(2) 114.38(11).

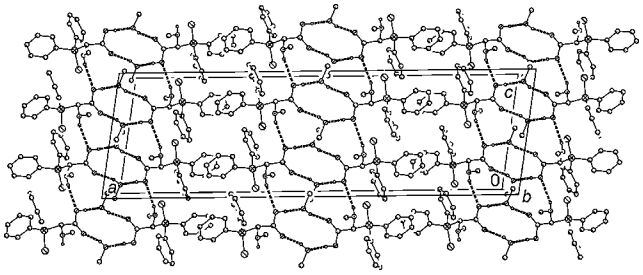


Figure 4. Packing of **6b** in the crystal (for clarity the *N*-(*p*-tolyl) group is represented only by the position of its *i*-C atom). The classic hydrogen bonds combine to form broad ribbons parallel to the *z* axis.

Structure and Behaviour in Solution

The structures of all the new compounds in solution were elucidated by reliable and complete sets of ^1H, ^{31}P and ^{13}C NMR spectroscopic data. Different chemical shift ranges of the P*CH* proton and ^{13}C nuclei distinguish the phosphanylglycine and phosphanylglycolate derivatives. A particular feature of the phosphanylglycines is the dynamic behaviour of the COO*H*, N*H* and PC*H* protons. The COO*H* signal is generally very broad and observable usually only by integration of the downfield region (below 8 ppm; see the Supporting Information). The appearance of the NH and CH signals depends on the N substituent and the temperature. Whereas the *N*-phenyl derivative **1a** in [D_8]THF displays separate broad N*H* and PC*H* singlets at room temperature and the less N-basic *p*-acetophenyl derivative **1c** doublets with $^3J_{HH}$ coupling, the more N-basic *p*-tolyl and *o*-hy-

droxyphenyl derivatives **1b** and **1d** show a very broad and flat N*H* signal and a broadened PC*H* peak. Variable-temperature ^{1}H NMR measurements of **1b** indicate that the higher basicity at the nitrogen atom causes the collapse of the $^3J_{HCNH}$ and $^2J_{PCH}$ fine-coupling at lower temperature.

The solution behaviour of **1b** was studied in more detail. At –50 °C doublets of doublets with $^3J_{HCNH}$ and $^2J_{PCH}$ couplings are observed for PC*H*, at –20 °C doublets and at 0 °C coalescence to two broad singlets (Figure 5). The N*H* signal becomes very broad and flat (visible by integration) on heating above room temperature, is symmetrically superimposed over the PC*H* signal at 40 °C and found slightly upfield at 55 °C. The PCH_2 doublet of **4b**, still very weak after 2 d at room temperature, increases rapidly on heating to 40 °C and particularly on heating to 55 °C and indicates the above-mentioned decarboxylation. The behaviour of **1b** in [D$_6$]DMSO is similar, but the line-broadening is slightly less, being comparable at 25 °C with that of **1b** in THF at 0 °C. A trace amount of an oxidation product is detectable by ^{31}P NMR (δ = 48 ppm) on heating at 40 and 55 °C, but no extensive oxidation by the sulfoxide solvent occurs. In the protic polar solvent CD_3OD the picture is different. The N*H* and PC*H* protons do not exhibit separate signals. Only a broad O*H* singlet of CD_3OH is visible, with a strong upfield shift with increasing temperature, as is known for methanol. N*H* and PC*H* protons undergo H/D exchange with the excess solvent. The exchange of the PC*H* proton by deuterium was confirmed by ^{13}C NMR spectroscopy. The α-*C*H signal of **1b** cannot be observed in CD_3OD because of H/D exchange. If a base such as *tert*-butylamine is added immediately to a freshly prepared solution of **1b**, the PCH signal is still observed, that is, complete PCH/PCD exchange is suppressed. The dynamic properties in solution in the absence of base are attributable to a rapid proton exchange on the NMR timescale between the acidic COOH and the Lewis basic amino or phosphanyl group. As shown by the PCH/PCD exchange in the deuterium donor solvent CD_3OD, even the usually rather weakly acidic α-CH proton is involved in quite rapid proton (deuterium) transfer reactions. Finally, it should be mentioned that the phosphorus signal of **1b** is only slightly different for the two solvents [D$_8$]THF and CD_3OD at room temperature (δ = –0.22 and 1.3 ppm) and little affected by the addition of excess glacial acetic acid (1:5 molar ratio, [D$_8$]THF: δ = –0.09 ppm; CD_3OD: δ = 1.3 ppm), pyridine ([D$_8$]THF: δ = –0.27 ppm; CD_3OD: δ = 0.7 ppm), or *tert*-butylamine (CD_3OD: δ = 1.5 ppm). This suggests that the extent of P-protonation in the equilibrium remains rather low despite the clear effects on the reactivity and stability of the α-phosphanyl amino acids.

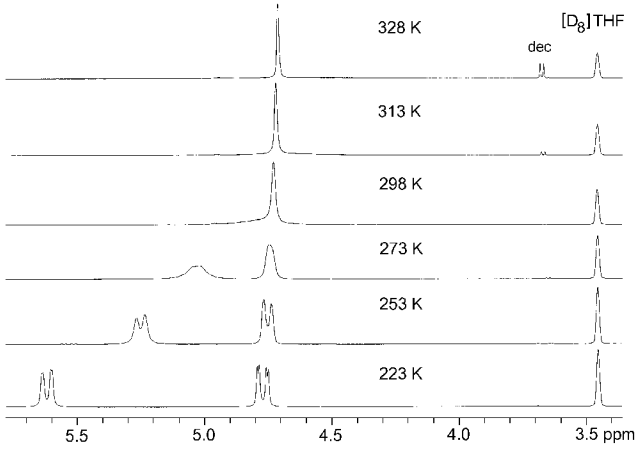


Figure 5. Variable-temperature proton signals of the N*H* and PC*H* nuclei of **1b** in [D$_8$]THF.

Conclusions

N-Aryl-α-phosphanylglycines, novel α-phosphanyl amino acids with reduced basicity at the nitrogen atom, are easily accessible by one-pot three-component reactions of primary arylamines, diphenylphosphane and glyoxylic acid hydrate in diethyl ether at room temperature. The reaction is restricted to *N*-monosubstituted amines and was found to involve intermediate arylammonium (diphenylphosphanyl)glycolates, which reversibly condense to the slightly more stable phosphanylglycines. Compared with conventional α-amino acids, the α-phosphanylglycines are much more sensitive to decarboxylation and hydrolysis. *N*-Aryl substituents are less sensitive to hydrolysis than *N*-alkylated phosphanylglycines and provide sufficient stabilization to allow an easy access to stable α-phosphinoylglycines by oxidation with aqueous hydrogen peroxide. [η^1-*P*-(Diphenylphosphanyl)glycineM(CO)$_5$] complexes, obtained by reaction of **1** with [M(CO)$_5$(THF)] (M = Cr, Mo, W), demonstrate the accessibility of phosphanylglycine transition-metal complexes and show that the phosphorus donor properties are comparable to those of the usual alkyldiphenylphosphanes. Although the electron lone-pair at phosphorus is blocked, the complexes remain sensitive to hydrolysis. Nevertheless, highly active catalysts for oligomerization of ethylene are formed in situ from THF solutions of the phosphanylglycines and Ni(cod)$_2$. The selectivity is the same as with the less easily accessible but hydrolytically more stable (diphenylphosphanyl)acetic acid ligand and hints at catalyst stabilization by a $\widehat{PO}^-$ nickel chelate backbone. The performance of the test ligands **1b** and **1c** in catalytic ethylene oligomerization suggests that exploring the transition-metal coordination and ways of stabilizing complexes of phosphanylglycines may reveal applications of the novel phosphanylglycine ligands in coordination chemistry and transition-metal-catalysed reactions.

Experimental Section

General: All manipulations with air-sensitive compounds were conducted under nitrogen using Schlenk techniques. Solvents were dried by standard methods and freshly distilled before use. NMR tubes of samples repeatedly measured over several days were closed by ground glass joints or sealed off to avoid slow oxidation by air diffusing through the usual plastic caps. Diphenylphosphane was prepared from triphenylphosphane by phenyl cleavage with sodium (2 equiv.) in liquid ammonia and neutralization with excess

NH_4Cl.[34] Other chemicals were purchased and used without further purification. NMR spectra were recorded with a multinuclear Bruker ARX300 FT-NMR spectrometer at 300.1 (^1H), 75.5 (^{13}C) and 121.5 (^{31}P) MHz. Chemical shifts (δ) are given in ppm and are referenced to tetramethylsilane for ^1H and ^{13}C NMR and to H_3PO_4 (85%) for ^{31}P NMR unless indicated otherwise. The relative intensities of the phosphorus signals do not represent quantitative molar ratios; they are used for rough estimations of the main, side and trace components or to observe changes in the relative concentration of a particular component. Coupling constants refer to J_{HH} (in ^1H NMR) or J_{PC} (in ^{13}C NMR) unless stated otherwise. Assignments of the C and H signals of the two *P*-phenyl groups, usually different by virtue of the asymmetric α-C atom, are indicated by *i*, *o*, *m* and *p* and by lower case $_A$ and $_B$. The C and H atoms of the *N*-aryl groups are denoted by either *i′*, *o′*, *m′* and *p′* or by numbers (N atom at C1). Elemental analyses were determined with a CHNS-932 analyser from LECO (standard conditions). Melting points (uncorrected) were measured in a capillary tube with a Sanyo Gallenkamp melting-point apparatus.

α-(Diphenylphosphanyl)-*N*-phenylglycine, MeOH Solvate (1a): A solution of glyoxylic acid monohydrate (0.5 g, 5.43 mmol) in diethyl ether (10 mL), best prepared in an ultrasound bath, was added to a solution of diphenylphosphane (1.0 g, 5.37 mmol) and aniline (0.50 g, 5.37 mmol) in diethyl ether (10 mL). After a few minutes precipitation of a white solid began. The mixture was stirred overnight, the solid filtered off, washed with diethyl ether and dried in vacuo to give a white powder (1.2 g, 67%), m.p. 119–121 °C. The compound was crystallized from methanol. ^1H NMR ([D$_8$]THF): δ = 4.88 (br. s, 1 H, PC*H*), 5.13 (very br. s, 1 H, N*H*), 6.59 (tt, ^3J = 7.2, ^4J = 0.9 Hz, 1 H, *p′*-C*H*), 6.66 (dt, ^3J = 8.4, ^4J = 0.9 Hz, 2 H, *o′*-C*H*), 7.04 (ddt, ^3J = 8.4, 7.2, ^4J = 1–2 Hz, 2 H, *m′*-C*H*), 7.24–7.35 (m, 6 H, Ph), 7.46–7.57 (m, 4 H, Ph), 3.26 (s, *Me*OH) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 58.06 (d, ^1J = 17.5 Hz, P*C*H), 114.32 (s, 2 *o′*-*C*H), 118.42 (s, *p′*-*C*H), 128.90 (d, ^3J = 7.0 Hz, 2 *m*-*C*H$_A$), 129.07 (d, ^3J = 12.9 Hz, 2 *m*-*C*H$_B$), 129.40 (s, *p*-*C*H$_A$), 129.56 (s, 2 *m′*-*C*H), 130.14 (s, *p*-*C*H$_B$), 133.57 (d, ^2J = 18.5 Hz, *o*-*C*H$_A$), 135.32 (d, ^2J = 21.2 Hz, *o*-*C*H$_B$), 136.13 (d, ^1J = 15.9 Hz, *i*-*C*$_{qA}$), 137.15 (d, ^1J = 17.2 Hz, *i*-*C*$_{qB}$), 148.43 (d, ^3J = 7.8 Hz, *i′*-*C*$_q$), 172.34 (d, ^2J = 9.3 Hz, *C*OOH), 49.82 (*Me*OH) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = –0.09 ppm. For the methanol solvate: $C_{21}H_{22}NO_3P$ (367.13): calcd. C 68.66, H 6.04, N 3.81; found C 68.62, H 5.98, N 3.62.

α-(Diphenylphosphanyl)-*N*-(*p*-tolyl)glycine (1b): A solution of glyoxylic acid monohydrate (0.60 g, 6.5 mmol) in diethyl ether (7 mL) was added to a solution of diphenylphosphane (1.21 g, 6.5 mmol) and *p*-toluidine (0.70 g, 6.5 mmol) in diethyl ether (15 mL). Work-up as described for **1a** furnished a white powder (2.2 g, 97%), m.p. 138–140 °C, that is soluble in methanol or THF, but at best sparingly soluble in water. Single crystals (colourless needles and columns) were obtained from a freshly prepared saturated solution in methanol. Crystal data are compiled in Table 2, selected bond lengths and angles are reported in Figure 2. ^1H NMR ([D$_8$]THF): δ = 2.05 (s, 3 H, C*H*$_3$), 4.73 (br. s, >3 H, PC*H*, N*H*, O*H*), 6.46 [m$_{(AA')}$, ^3J = 8.4 Hz, 2 H, *o′*-C*H*], 6.76 [m$_{(BB')}$, $^3J \approx$ 8.2 Hz, 2 H, *m′*-C*H*], 7.15–7.23 (m, 6 H, *o*-C*H*, *p*-C*H*), 7.36–7.45 (m, 4 H, *m*-C*H*), 3.15 (s, 0.1 MeOH) ppm. ^1H NMR ([D$_6$]DMSO): δ = 2.14 (s, 3 H, C*H*$_3$), 4.87 (br. s, 1 H, PC*H*), 5.69 (very br. s, N*H*), 6.65 [m$_{(AA')}$, ^3J = 8.4 Hz, 2 H, *o′*-C*H*], 6.89 [m$_{(BB')}$, $^3J \approx$ 8.3 Hz, 2 H, *m′*-C*H*], 7.33–7.43 (m, 6 H, *o*-C*H*, *p*-C*H*), 7.45–7.55 (m, 4 H, *m*-C*H*), 12.30 (very br. s, 1 H, COO*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]-THF): δ = 20.42 (s, C*H*$_3$), 58.31 (d, ^1J = 17.6 Hz, P*C*H), 114.46 (*o′*-*C*H), 127.26 (*p′*-*C*$_q$), 128.83 (d, ^3J = 7.4 Hz, *m*-*C*H$_A$), 128.99 (d, ^3J = 5.4 Hz, *m*-*C*H$_B$), 129.29 (s, *p*-*C*H$_A$), 130.02 (s, 2 *m′*-*C*H), 130.06 (s, *p*-*C*H$_B$), 133.53 (d, ^2J = 17.8 Hz, 2 *o*-*C*H$_A$), 135.31 (d, ^2J = 21.6 Hz, 2 *o*-*C*H$_B$), 136.24 (d, ^1J = 15.9 Hz, *i*-*C*$_{qA}$), 137.28 (d, ^1J = 17.9 Hz, *i*-*C*$_{qB}$), 146.17 (d, ^3J = 7.6 Hz, *i*-*C*$_q$′), 172.37 (d, ^2J = 9.5 Hz, *C*OOH) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 0.22 ppm. IR (KBr disc): $\tilde{\nu}$ = 3368 (m), 3051 (m), 2917 (m), 2611 (mw), 2534 (mw), 1698 (vs), 1614 (m), 1514 (s), 1481 (m), 1432 (m), 1292 (m), 1264 (s), 817 (s), 743 (s), 696 (s) cm^{-1}. $C_{21}H_{20}NO_2P$ (349.36): calcd. C 72.20, H 5.77, N 4.01; found C 72.27, H 5.48, N 3.81.

α-(Diphenylphosphanyl)-*N*-(4-acetylphenyl)glycine Methanol Solvate (1c): A solution of glyoxylic acid monohydrate (0.50 g, 5.43 mmol) in diethyl ether (10 mL) was added to a solution of diphenylphosphane (1.01 g, 5.4 mmol) and 4-aminoacetophenone (0.73 g, 5.4 mmol) in diethyl ether (10 mL). Work-up as described for **1a** furnished a white powder (1.1 g, 54%), m.p. 104–106 °C. The substance is easily soluble in methanol and crystallizes in the form of needles when the solution is concentrated. ^1H NMR ([D$_8$]THF): δ = 2.36 (s, 3 H, C*H*$_3$), 5.01 (d, J = 9.1 Hz, 1 H, PC*H*), 6.00 (d, J = 8.1 Hz, 1 H, N*H*), 6.69 [m$_{(AA')}$, 2 H, *o′*-C*H*], 7.24–7.38 (m, 6 H, Ph*H*), 7.45–7.58 (m, 4 H, Ph*H*), 7.73 [m$_{(BB')}$, 2 H, *m′*-C*H*] ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 25.79 (s, *C*H$_3$), 57.67 (d, ^1J = 19.1 Hz, P*C*H), 113.02 (s, 2 *o′*-*C*H), 128.44 (s, *p′*-*C*$_q$), 128.96 (d, ^3J = 7.8 Hz, 2 *m*-*C*H$_A$), 129.24 (d, ^3J = 6.5 Hz, 2 *m*-*C*H$_B$), 129.67 (s, *p*-*C*H$_A$), 130.25 (s, *p*-*C*H$_B$), 130.88 (s, 2 *m′*-*C*H), 133.73 (d, ^2J = 19.0 Hz, 2 *o*-*C*H$_A$), 135.27 (d, ^2J = 21.3 Hz, 2 *o*-*C*H$_B$), 135.89 (d, ^1J = 16.3 Hz, *i*-*C*$_{qA}$) 136.72 (d, ^1J = 16.7 Hz, *i*-*C*$_{qB}$), 152.20 (d, ^3J = 6.6 Hz, *i′*-*C*$_q$), 171.63 (d, ^2J = 8.9 Hz, *C*OOH), 194.51 (s, *C*O) ppm. ^{31}P NMR ([D$_8$]THF): δ = 0.24 ppm. For methanol solvate: $C_{23}H_{24}NO_4P$ (409.14): calcd. C 67.47, H 5.91, N 3.42; found C 67.21, H 6.19, N 3.63.

α-(Diphenylphosphanyl)-*N*-(2-hydroxyphenyl)glycine (1d): A solution of glyoxylic acid monohydrate (0.50 g, 5.43 mmol) in diethyl ether (20 mL) was added to a solution of diphenylphosphane (1.0 g, 5.37 mmol) and *o*-aminophenol (0.59 g, 5.4 mmol) in diethyl ether (5 mL). Work-up as described for **1a** furnished a white powder (1.51 g, 80%), m.p. 110–115 °C. ^1H NMR ([D$_8$]THF): δ = 4.87 (s, 1 H, PC*H*), 6.35–6.64 (m, 4 H, 3′-C*H* to 6′-C*H*), 7.25–7.34 (m, 6 H, Ph*H*), 7.41–7.58 (m, 4 H, Ph*H*) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 57.70 (d, ^1J = 19.6 Hz, P*C*H), 111.98 (s, 6-*C*H), 114.23 (s, 3-*C*H), 118.00 (s, 4-*C*H), 120.53 (s, 5-*C*H), 128.83 (d, ^3J = 7.3 Hz, *m*-*C*H$_A$), 128.95 (d, ^3J = 5.7 Hz, *m*-*C*H$_B$), 129.34 (s, *p*-*C*H$_A$), 129.91 (s, *p*-*C*H$_B$), 133.89 (d, ^2J = 18.8 Hz, *o*-*C*H$_A$), 135.07 (d, ^2J = 21.2 Hz, *o*-*C*H$_B$), 136.32 (d, ^1J = 16.5 Hz, *i*-*C*$_{qA}$), 136.83 (d, ^1J = 18.6 Hz, *i*-*C*$_{qB}$), 137.05 (d, ^3J = 6.1 Hz, 1-*C*$_q$), 145.70 (s, 2-*C*$_q$), 172.17 (d, ^2J = 8.1 Hz, *C*OOH) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 0.99 ppm. $C_{20}H_{18}NO_3P$ (351.10): calcd. C 68.37, H 5.16, N 3.99; found C 68.59, H 4.81, N 3.70.

***N*-Methylanilinium (Diphenylphosphanyl)glycolate (3):** A solution of glyoxylic acid monohydrate (0.50 g, 5.43 mmol) in diethyl ether (20 mL) was added to a solution of diphenylphosphane (1.00 g, 5.37 mmol) and *N*-methylaniline (580 mg, 5.41 mmol) in diethyl ether (15 mL). Work-up as described for **1a** furnished a white powder (1.60 g, 86%), m.p. 89–93 °C. ^1H NMR ([D$_8$]THF): δ = 2.89 (very br., 6 H, C*H*$_3$, 3 N*H*/O*H*), 5.07 (d, $^2J_{PH}$ = 2.5 Hz, 1 H, PC*H*O), 6.60 (tt, ^3J = 7.3 Hz, 1 H, *p′*-C*H*), 6.69 (m, ^3J = 7–8 Hz, 2 H, *o′*-C*H*), 7.12 (m, ^3J = 8.8, 7.3 Hz, 2 H, *m′*-C*H*), 7.24–7.33 (m, Ph*H*), 7.42–7.61 (m, Ph*H*) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 40.50 (s, *C*H$_3$), 73.02 (d, $^1J_{PC}$ = 26.0 Hz, P*C*HO), 113.18 (s, 2 *o′*-*C*H), 117.00 (s, *p′*-CH), 128.64 (d, $^3J_{PC}$ = 6.7 Hz, 2 *m*-*C*H$_A$), 128.72 (d, $^3J_{PC}$ = 6.9 Hz, 2 *m*-*C*H$_B$), 129.31 (s, *p*-*C*H$_A$), 129.38 (s, 2 *m′*-*C*H, *p*-*C*H$_B$), 134.65 (d, $^2J_{PC}$ = 19.9 Hz, 2 *o*-*C*H$_A$), 134.81 (d, $^2J_{PC}$ = 18.7 Hz, 2 *o*-*C*H$_B$), 136.14 (d, $^1J_{PC}$ = 17.2 Hz, *i*-*C*$_{qA}$), 137.19 (d, $^1J_{PC}$ = 14.7 Hz, *i*-*C*$_{qB}$), 151.61 (s, *i*-*C*$_q$′), 174.28

(d, $^2J_{PC}$ = 10.7 Hz, *C*OOH) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 6.44 ppm. $C_{21}H_{22}NO_3P$ (367.38): calcd. C 68.66, H 6.04, N 3.81; found C 68.56, H 6.02, N 4.02. (A small amount of Ph_2PH was detected, increasing with the time because of slow protolytic P–C cleavage in solution.).

Thermal Decarboxylation of 1b and Detection of *N*-[(Diphenylphosphanyl)methyl]-*p*-toluidine (4b) and its Oxide 4b(O): Neat **1b** (0.759 g, 2.17 mmol) was heated in a Schlenk flask at 95 °C. After 2 h the solid had turned to a pale-yellow melt that formed a viscous liquid at room temperature. ^{31}P NMR monitoring in [D$_8$]THF showed the formation of **4b**, $(Ph_2PCH_2)_2NpTol$[24] (δ = –27.0) and a trace of Ph_2PH (δ = –40.6 ppm), relative intensities 82:17:1. Replacement of [D$_8$]THF by CD_3OD gave similar shifts for **4b** and $(Ph_2PCH_2)_2NpTol$ (δ = –20.2, –26.6 ppm) and no hint of reaction of either compound with methanol. The mixture was oxidized by air and worked up by column chromatography to give 0.42 g (60%) of **4b(O)**.

4b: ^1H NMR ([D$_8$]THF): δ = 2.06 (s, 3 H, C*H*$_3$), 3.67 (d, ^2J = 4.1 Hz, 2 H, PC*H*$_2$), 6.45 [m$_{(AA')}$, ^3J = 8.5 Hz, 2 H, *o*′-C*H*], 6.76 [m$_{(BB')}$, $^3J \approx$ 8.1 Hz, 2 H, *m*′-C*H*], 7.13–7.23 (m, 6 H, *o*-C*H*, *p*-C*H*), 7.28–7.37 (m, 4 H, *m*-C*H*) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 20.45 (s, C*H*$_3$), 45.31 (d, ^1J = 9.0 Hz, PC*H*$_2$N), 113.51 (*o*′-*C*H), 126.06 (*p*′-*C*$_q$), 129.17 (d, ^3J = 6.7 Hz, *m*-*C*H), 129.29 (s, *p*-*C*H), 129.93 (s, 2 *m*′-*C*H), 133.57 (d, ^2J = 18.5 Hz, 2 *o*-*C*H), 138.69 (d, ^1J = 14.7 Hz, *i*-*C*$_q$), 147.46 (d, ^3J = 6.1 Hz, *i*-*C*$_q$′) ppm. $^{31}P\{^1H\}$ ([D$_8$]THF): δ = –20.7 ppm.

4b(O): ^1H NMR (CD_3OD): δ = 2.16 (s, 3 H, C*H*$_3$), 4.12 (d, ^2J = 6.0 Hz, 2 H, PC*H*$_2$), 6.58 [m$_{(AA')}$, ^3J = 8.5 Hz, 2 H, *o*′-C*H*], 6.87 [m$_{(BB')}$, $^3J \approx$ 8.1 Hz, 2 H, *m*′-C*H*], 7.26–7.64 (m, 6 H, *m*-C*H*, *p*-C*H*), 7.82 (m, $^3J_{PH}$ = 11.5, ^3J = 8.0–8.4 Hz, 4 H, *o*-C*H*) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR (CD_3OD): δ = 20.48 (s, C*H*$_3$), 45.43 [d, ^1J = 82.1 Hz, P(O)*C*H$_2$N], 114.55 (*o*′-*C*H), 128.24 (*p*′-*C*$_q$), 129.99 (d, ^3J = 11.9 Hz, *m*-*C*H), 130.44 (s, 2 *m*′-*C*H), 131.95 (d, ^1J = 99.1 Hz, *i*-*C*$_q$), 132.35 (d, ^2J = 9.3 Hz, 2 *o*-*C*H), 133.66 (d, ^4J = 2.5 Hz, *p*-*C*H), 147.11 (d, ^3J = 7.8 Hz, *i*-*C*$_q$′) ppm. $^{31}P\{^1H\}$ (CD_3OD): δ = 32.2 ppm. HRMS (ESI in MeOH): calcd. for $C_{20}H_{21}NOP$ [M + H]$^+$ 322.13553; found 322.13574.

α-(Diphenylphosphinoyl)-*N*-(*p*-tolyl)glycine, Methanol Solvate (5b): Glycine **1b** (500 mg, 1.43 mmol) was added to excess aqueous H_2O_2 (10 mL, 30%) and the mixture shaken at room temperature for 1 d. The solution was concentrated in vacuo, the resulting precipitate was separated by filtration, washed with methanol (3 mL) and dried in vacuo to give a white powder (529 mg, 93%), m.p. 162–163 °C. ^1H NMR ([D$_8$]THF): δ = 2.14 (s, 3 H, C*H*$_3$), 5.10–5.23 (m, 2 H, PC*H*, N*H*), 6.61 (d, $^3J_{PH}$ = 8.4 Hz, 2 H, *o*′-C*H*), 6.85 (d, $^3J_{PH}$ = 8.3 Hz, 2 H, *m*′-C*H*), 7.37–7.53 (m, 6 H, Ph*H*), 7.85–8.00 (m, 4 H, Ph*H*), 3.26 (s, 3 H, *Me*OH) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 20.43 (s, C*H*$_3$), 59.12 (d, ^1J = 70.4 Hz, PCH), 114.86 (2 *o*′-*C*H), 127.92 (*p*′-*C*H), 128.81 (d, ^3J = 12.1 Hz, 2 *m*-*C*H$_A$), 129.04 (d, ^3J = 12.0 Hz, 2 *m*-*C*H$_B$), 129.98 (2 *m*′-*C*H), 132.20 (d, ^1J = 99.6 Hz, *i*-*C*$_{qA}$), 132.32 (d, ^2J = 9.3 Hz, 2 *o*-*C*H$_A$), 132.48 (d, ^4J = 2.7 Hz, *p*-*C*H$_A$), 132.56 (br., superimposed, *p*-*C*H$_B$), 132.78 (d, ^2J = 9.3 Hz, 2 *o*-*C*H$_B$), 132.72 (d, ^1J = 101.1 Hz, *i*-*C*$_{qB}$), 145.98 (d, ^3J = 11.6 Hz, *i*′-*C*$_q$), 169.93 (s, *C*OOH), 49.77 (MeOH) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 27.49 ppm. IR (KBr disc): $\tilde{\nu}$ = 3432 (vs), 1635 (m), 1606 (m), 1592 (m), 1437 (s), 1249 (m), 1178 (vs), 1164 (vs), 1124 (s), 887 (s), 741 (vs), 695 (vs) cm^{-1}. MS (EI, 70 eV, 315 °C): *m*/*z* (%) = 322 (2), 321 (9) [M – CO_2]$^+$, 202 (24) [Ph_2PO]$^+$, 120 (100) [TolNHCH$_2$]$^+$, 91 (19), 47 (17). For the methanol solvate: $C_{22}H_{24}NO_4P$ (397.40): calcd. C 66.49, H 6.09, N 3.52; found C 66.47, H 6.06, N 3.59.

α-(Diphenylphosphinoyl)-*N*-(4-acetylphenyl)glycine (5c): A mixture of **1c** (635 mg, 1.68 mmol) and aqueous H_2O_2 (15 mL, 30%) was stirred for 1 d at room temperature. The resulting small white needles were separated, washed with methanol (3 mL) and dried in vacuo (609 mg, 92%), m.p. 151–154 °C. ^1H NMR ([D$_8$]THF): δ = 2.36 (s, 3 H, C*H*$_3$), 5.41 (dd, $^2J_{PH}$ = 11.8, ^3J = 10.5 Hz, 1 H, PC*H*), 6.39 (dd, ^3J = 10.2, $^3J_{PH}$ = 3.9 Hz, 1 H, N*H*), 6.75 [m$_{(AA')}$, ^3J = 8.8 Hz, 2 H, *o*′-C*H*], 7.37–7.56 (m, 6 H, Ph*H*), 7.69 [m$_{(BB')}$, ^3J = 8.8 Hz, 2 H, *m*′-C*H*], 7.86–8.02 (m, 4 H, Ph*H*) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 25.87 (s, *C*H$_3$), 58.14 (d, ^1J = 68.7 Hz, P*C*H), 113.23 (2 *o*′-*C*H), 128.50 (*p*′-*C*$_q$), 129.55 (d, ^3J = 12.7 Hz, 2 *m*-*C*H$_A$), 129.30 (d, ^3J = 12.2 Hz, 2 *m*-*C*H$_B$), 130.90 (s, 2 *m*′-*C*H), 131.32 (d, ^1J = 99.8 Hz, *i*-*C*$_{qA}$), 131.95 (d, ^1J = 102.2 Hz, *i*-*C*$_{qB}$), 132.11 (d, ^2J = 9.4 Hz, 2 *o*-*C*H$_A$), 132.57 (d, ^2J = 9.4 Hz, 2 *o*-*C*H$_B$), 132.87 (d, ^4J = 2.3 Hz, *p*-*C*H$_A$), 132.94 (d, ^4J = 2.6 Hz, *p*-*C*H$_B$), 152.44 (d, ^3J = 8.2 Hz, *i*′-*C*$_q$), 169.56 (s, *C*OOH), 195.92 (s, *C*O) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 29.92 ppm. IR (KBr disc): $\tilde{\nu}$ = 3431 (vs), 1640 (vs), 1586 (vs), 1405 (s), 1282 (m), 1139 (wm), 821 (wm) cm^{-1}. $C_{22}H_{20}NO_4P$ (393.37): calcd. C 67.17, H 5.12, N 3.56; found C 66.90, H 5.10, N 3.48.

α-(Diphenylthiophosphinoyl)-*N*-(*p*-tolyl)glycine, Methanol Solvate (6b): A mixture of equimolar amounts of **1b** (310 mg, 0.89 mmol) and sulfur (28.5 mg, 0.89 mmol) in methanol (10 mL) was stirred for 1 d at room temperature. Then about 50% of the solvent was evaporated in vacuo, yielding small white needles. These were separated by filtration, washed with methanol and briefly dried (308 mg, 84%), m.p. 77–83 °C. The compound is soluble in THF, water and to a lesser extent in methanol. A single crystal of the methanol solvate suitable for X-ray diffraction (for crystal data see Table 2, selected bond lengths and angles are reported in Figure 3) was taken directly from the methanol mother liquor. ^1H NMR integration of freshly prepared **6b** confirms a 1:1 ratio of **6b**/methanol. On storage the substance loses some methanol. ^1H NMR ([D$_8$]-THF): δ = 2.05 (s, 3 H, C*H*$_3$), ca. 1.5–2.70 and 2.70–3.00 (br. s, 2 H, O*H*), 4.87 [br. dd, $^3J_{(HCNH)}$ = 11.2, $^3J_{(PH)}$ = 4.9 Hz, 1 H, N*H*], 5.35 [dd, $^2J_{(PH)}$ = 13.4, $^3J_{(HCNH)}$ = 11.2 Hz, 1 H, PC*H*], 6.51 [m$_{(AA')}$, $^3J \approx$ 8.4 Hz, 2 H, 2 *o*′-C*H*], 6.76 [m$_{(BB')}$, $^3J \approx$ 8.3 Hz, 2 H, 2 *m*′-C*H*], 7.23–7.42 (m, 6 H, 4 *m*-C*H*, 2 *p*-C*H*), 7.81–7.90 [m, $^3J_{(PH)}$ = 12.8 Hz, 2 H, *o*-C*H*$_A$], 7.93–8.02 [m, $^3J_{(PH)}$ = 13.2 Hz, 2 H, *o*-C*H*$_B$], 11.15 (br. s, OH), 3.15 (s, 3 H, *Me*OH) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 19.15 (*p*′-*C*H$_3$), 48.51 (*Me*OH), 57.78 (d, ^1J = 56.7 Hz, P*C*H), 113.75 (2 *o*′-*C*H), 126.94 (*p*′-*C*$_q$), 127.32 (d, ^3J = 13.0 Hz, 2 *m*-*C*H$_A$), 127.66 (d, ^3J = 12.8 Hz, 2 *m*-*C*H$_B$), 128.79 (s, 2 *m*′-*C*H), 130.68 (d, ^1J = 78.0 Hz, *i*-*C*$_{qA}$), 130.75 (d, ^4J = 2.6 Hz, *p*-*C*H$_A$), 130.98 (d, ^4J = 2.7 Hz, *p*-*C*H$_B$), 131.13 (d, ^2J = 9.6 Hz, 2 *o*-*C*H$_A$), 132.07 (d, ^2J = 10.5 Hz, *o*-*C*H$_B$), 132.14 (d, ^1J = 83.2 Hz, *i*-*C*$_{qB}$), 144.18 (d, ^3J = 11.9 Hz, *i*′-*C*$_q$), 167.69 (d, ^2J = 5.1 Hz, *C*OOH) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 46.5 ppm. $C_{21}H_{20}NO_2PS$ (381.43): calcd. C 66.13, H 5.29, N 3.67. For the methanol solvate: $C_{22}H_{24}NO_3PS$ (413.47): calcd. C 63.91, H 5.85, N 3.39; found C 65.74, H 5.59, N 3.46.

α-(Diphenylthiophosphinoyl)-*N*-(4-acetylphenyl)glycine (6c): A mixture of equimolar amounts of **1c** (630 mg, 1.67 mmol) and sulfur (53.4 mg, 1.67 mmol) in methanol (10 mL) was stirred for 1 d at room temperature and filtered. Then about 50% of the solvent was evaporated in vacuo to give small white needles that were separated, washed with methanol (5 mL) and dried (649 mg, 95%), m.p. 164–165 °C. ^1H NMR ([D$_8$]THF): δ = 2.36 (s, 3 H, C*H*$_3$), 5.70 [dd, $^2J_{(PH)}$ = 12.2, $^3J_{(HCNH)}$ = 10.6 Hz, 1 H, PC*H*], 5.90 [dd, $^3J_{(HCNH)}$ = 10.6, $^3J_{(PH)}$ = 4.3 Hz, 1 H, N*H*], 6.73 [m$_{(AA')}$, $^3J \approx$ 8.8 Hz, 2 H, *o*′-C*H*], 7.32–7.52 (m, Ph*H*), 7.69 [m$_{(BB')}$, $^3J \approx$ 8.8 Hz, 2 H, *m*′-C*H*], 7.92 (m, 4 H, Ph*H*), 3.26 (s, 0.3 H, *Me*OH) ppm. $^{13}C\{^1H\}$ and DEPT-135 NMR ([D$_8$]THF): δ = 25.75 (s, *C*H$_3$), 58.11 (d, ^1J

= 54.4 Hz, PCH), 113.33 (2 *o′*-*C*H), 128.66 (d, ^3J = 12.9 Hz, 2 *m*-CH_A), 128.97 (*p′*-C_q), 129.00 (d, ^3J = 12.0 Hz, 2 *m*-CH_B), 130.70 (s, 2 *m′*-*C*H), 131.67 (partially superimposed d, $^1J \approx 80$ Hz, *i*-C_{qA}), 132.25 (d, ^4J = 3.9 Hz, *p*-CH_A), 132.39 (d, ^4J = 3.8 Hz, *p*-CH_B), 132.40 (d, ^2J = 10.0 Hz, 2 *o*-CH_A), 132.75 (partially superimposed d, $^1J \approx 80$ Hz, *i*-C_{qA}), 133.30 (d, ^2J = 10.6 Hz, 2 *o*-CH_B), 151.58 (d, ^3J = 8.1 Hz, *i′*-C_q), 168.29 (d, ^2J = 4.0 Hz, *C*OOH), 194.68 (s, *C*O), 49.77 (*Me*OH) ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 47.3 ppm. $C_{22}H_{20}NO_3PS$ (409.44): calcd. C 64.54, H 4.92, N 3.42; found C 64.44, H 4.77, N 3.33.

η^1-*P*-[α-(Diphenylphosphanyl)-*N*-(*p*-tolyl)glycine](pentacarbonyl)-chromium(0) (7b): [Cr(CO)$_6$] (375 mg, 1.70 mmol) was dissolved in THF (85 mL) and irradiated with a UV immersion lamp until the calculated amount of CO had been liberated (3 h). Solid **1b** (650 mg, 1.86 mmol) was then added to the resulting yellow solution of [Cr(CO)$_5$(THF)]. After stirring for 30 min most of the solvent was evaporated in vacuo to leave a residual volume of around 5 mL. CH_2Cl_2 (25 mL) was added, insoluble material filtered off and the solution stored overnight at –20 °C. The small, pale-yellow crystals that formed were separated from the cold solution and dried in vacuo (775 mg, 75%). The substance was contaminated by a small amount of **1b** [$\delta(^{31}P)$ = 2.8 ppm] and [Cr(CO)$_6$] [$\delta(^{13}C)$ = 211.5 ppm]. ^1H NMR ($CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 5.07 (br., 1 H, PC*H*), 6.60 (br., 2 H, *o′*-C*H*), 6.99 (br., 2 H, *m′*-C*H*), 7.20–7.80 (m, 10 H, 2 Ph*H*), 8.5–9.5 (br. s, 1 H, OH) ppm; NH superimposed. $^{13}C\{^1H\}$ and DEPT-135 NMR ($CDCl_3$): δ = 20.45 (*p′*-CH_3), 58.73 (d, ^1J = 15.8 Hz, P*C*H), 114.57 (s, 2 *o′*-*C*H), 128.56 (d, $^3J \approx 8.7$ Hz, 2 *m*-CH_A), 128.67 (d, ^3J = 7.8 Hz, 2 *m*-CH_B), 129.23 (s, *p′*-C_q), 129.92 (s, 2 *m′*-*C*H), 130.63 (s, *p*-CH_A), 130.78 (s, *p*-CH_B), 132.52 (d, ^2J = 10.2 Hz, 2 *o*-CH_A), 132.78 (d, ^2J = 10.8 Hz, 2 *o*-CH_B), 132.68 (d, $^1J \approx 34$ Hz, *i*-C_{qA}), 133.47 (d, ^1J = 32.4 Hz, *i*-C_{qB}), 143.66 (d, ^3J = 8.2 Hz, *i′*-C_q), 171.69 (d, ^2J = 6.2 Hz, *C*OOH), 216.21 (d, ^2J = 12.8 Hz, 4 *cis*-*C*O), 221.32 (d, ^2J = 5.2 Hz, *trans*-*C*O) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 65.04 ppm. IR (KBr disc): $\tilde{\nu}$ = 3419 (m, br.), 2064 (wm), 1985 (w), 1940 (vst), 1698 (s), 1615 (m), 1516 (s), 696 (m) cm^{-1}. $C_{26}H_{20}CrNO_7P$ (541.41): calcd. C 57.68, H 3.74, N 2.59; found C 58.12, H 3.58, N 2.45.

η^1-*P*-[α-(Diphenylphosphanyl)-*N*-(*p*-tolyl)glycine](pentacarbonyl)molybdenum(0) (8b): [Mo(CO)$_6$] (283 mg, 1.07 mmol) was dissolved in THF (85 mL) and irradiated with a UV immersion lamp until the calculated amount of CO had been liberated (2.5 h, repeated replacement of CO by N_2). Solid **1b** (400 mg, 1.14 mmol) was added to the resulting yellow solution of [Mo(CO)$_5$(THF)]. After stirring for 30 min the solvent was evaporated in vacuo. The residue was taken up in THF (2 mL) and CH_2Cl_2 (10 mL) was added. After 4 h at –20 °C small yellow crystals had formed that were separated, washed with CH_2Cl_2 and dried in a vacuum (509 mg, 76%). ^1H NMR ($CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 4.01 (br. s, 1 H, N*H*), 4.95 (br. s, 1 H, PC*H*), 6.61 (d, ^3J = 7.8 Hz, 2 H, *o′*-C*H*), 7.04 (d, ^3J = 7.7 Hz, 2 H, *m′*-C*H*), 7.37–7.50 (m, 6 H, Ph*H*), 7.55–7.65 (m, 4 H, Ph*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.45 (s, *C*H$_3$), 58.88 (d, ^1J = 14.4 Hz, P*C*H), 114.57 (s, 2 *o′*-*C*H), 128.70 (d, ^3J = 9.3 Hz, 2 *m*-CH_A), 128.73 (d, ^3J = 9.3 Hz, 2 *m*-CH_B), 129.68 (s, *p′*-C_q), 130.03 (s, 2 *m′*-*C*H), 130.59 (s, *p*-CH_A), 131.00 (s, *p*-CH_B), 132.18 (d, ^2J = 11.8 Hz, 2 *o*-CH_A), 132.32 (d, ^1J = 33.0 Hz, *i*-C_{qA}), 133.11 (d, ^2J = 12.2 Hz, 2 *o*-CH_B), 134.00 (d, ^1J = 33.0 Hz, *i*-C_{qB}), 143.26 (d, ^3J = 8.8 Hz, *i′*-C_q), 172.23 (d, ^2J = 6.5 Hz, *C*OOH), 204.02 (d, ^2J = 9.1 Hz, 4 *cis*-*C*O) ppm; *trans*-*C*O in noise. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 46.8 ppm. IR (KBr disc): $\tilde{\nu}$ = 3435 (s, br.), 2073 (wm), 1977, 1951 (vs), 1636 (m), 1436 (w), 590 (s) cm^{-1}. $C_{26}H_{20}MoNO_7P$ (585.35): calcd. C 53.35, H 3.44, N 2.39; found C 53.60, H 3.24, N 2.24. [If a solution of **1b** in THF was added to the solution of [Mo(CO)$_5$(THF)], ^{31}P NMR reaction monitoring indicated the presence of impurities (δ = 6.7 ppm and smaller signals) in addition to the main product (δ = 46.1 ppm)].

η^1-*P*-[α-(Diphenylphosphanyl)-*N*-(*p*-tolyl)glycine](pentacarbonyl)-tungsten(0) (9b): [W(CO)$_6$] (380 mg, 1.08 mmol) was dissolved in THF (80 mL) and irradiated with a UV immersion lamp until the calculated amount of CO had been liberated (3.5 h). Solid **1b** (190 mg, 0.54 mmol) was added to the solution of [W(CO)$_5$(THF)]. After stirring for 3 h, the solvent was partially evaporated in vacuo (residual volume ca. 5 mL). CH_2Cl_2 (15 mL) was added, the insoluble residue was filtered off and the solution was stored for 3 d at –24 °C. Small, pale-yellow crystals formed that were separated from the cold mother liquor, washed with CH_2Cl_2 (5 mL) and dried in vacuo (227 mg, 62%). ^1H NMR ($CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 5.02 [d, $^2J_{(PH)}$ = 9.4 Hz, 1 H, PC*H*], 6.61 [$m_{(AA')}$, ^3J = 8.4 Hz, 2 H, *o′*-C*H*], 7.00 [$m_{(BB')}$, $^3J \approx 8.2$ Hz, 2 H, *m′*-C*H*], 7.36–7.51 (m, 6 H, Ph*H*), 7.54–7.68 (m, 4 H, Ph*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.43 (s, *C*H$_3$), 59.36 (d, ^1J = 20.2 Hz, P*C*H), 114.61 (s, 2 *o′*-*C*H), 128.56 (d, ^3J = 9.6 Hz, 2 *m*-CH_A), 128.63 (d, ^3J = 10.1 Hz, 2 *m*-CH_B), 129.37 (s, *p′*-C_q), 129.94 (s, *m′*-*C*H), 130.69 (d, ^4J = 1.6 Hz, *p*-CH_A), 130.98 (br. s, *p*-CH_B), 132.41 (d, ^2J = 11.0 Hz, 2 *o*-CH_A), 132.47 (d, ^1J = 39.5 Hz, *i*-C_{qA}), 133.23 (d, ^2J = 11.8 Hz, 2 *o*-CH_B), 133.88 (d, ^1J = 38.3 Hz, *i*-C_{qB}), 143.38 (d, ^3J = 9.2 Hz, *i′*-C_q), 171.36 (d, ^2J = 7.0 Hz, *C*OOH), 196.47 (d, satellite, ^2J = 7.4, $^1J_{WC}$ = 126.0 Hz, 4 *cis*-*C*O), 198.75 (d, ^2J = 24.0 Hz, 1 *trans*-*C*O) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.4 ($^1J_{PW}$ = 249.4 Hz) ppm. IR (KBr disc): $\tilde{\nu}$ = 3437 (s, br.), 2071 (wm), 1973, 1938 (vs), 1634 (m), 1437 (w), 695 (m), 580 (ms) cm^{-1}. $C_{26}H_{20}NO_7PW$ (673.25): calcd. C 46.38, H 2.99, N 2.08; found C 46.44, H 2.91, N 2.02.

Oligo/Polymerization of Ethylene: The various phosphanylglycines **1** (see Table 1) and Ni(cod)$_2$ (each ca. 100 μmol) were dissolved in THF or toluene (10 mL), cooled to 0 °C (10 min) and mixed. The resulting yellow-brown solution was stirred at room temperature for 5 min and transferred through a Teflon® tube to the argon-filled autoclave. After weighing, the autoclave was pressurized with ethylene (30–50 bar), the amount of ethylene was determined and the autoclave was placed in the silicon bath and heated overnight (15 h) at 100 ± 5 °C. After cooling to room temperature unconverted ethylene was allowed to escape through a cooling trap (–40 °C; only trace amounts of butenes were observed). The volatiles were flash-distilled at 80 °C/4.0 mbar from the solvent product mixture. The residual waxy oligomer or polymer was treated for 1 d with methanol/hydrochloric acid (1:1), thoroughly washed with methanol and finally dried in vacuo. The density was determined by the sinking method using polymer tablets (IR press, 10 kbar) in water/ethanol. The results are compiled in Table 1. The microstructure and molecular weights of the polyethylene waxes were determined by ^1H NMR at 100 °C in C_6D_5Br after swelling for 1 d under argon at 100 °C (acquisition time 4.9–5.4 s, delay 1.0 s). The strong preference for linear chains with vinyl and methyl end groups was also confirmed in two control experiments by ^{13}C NMR measurements {acquisition time 0.6–0.9 s, delay 0.1–0.4 s, presence of 3–5 mg [Cr(acac)$_3$]}. The reference was the *p*-CH of the solvent: $\delta(^1H)$ = 7.23 ppm, $\delta(^{13}C)$ = 126.70 ppm.

Crystal Structure Analyses: X-ray diffraction data for **1b** and **6b** were recorded with an Oxford Diffraction Nova A diffractometer using mirror-focussed Cu-K_α radiation. The structures were refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97).[35] The NH and OH hydrogen atoms were refined freely; other hydrogen atoms were calculated by assuming idealized geometries and refined by using riding models or rigid methyl groups. Crystallographic data are given in Table 2 and selected bond lengths and angles are presented in Figures 2 and 3. CCDC-

743854 (for **1b**) and -743855 (for **6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement for **1b** and **6b**·MeOH.

Compound	**1b**	**6b**·MeOH
Empirical formula	$C_{21}H_{20}NO_2P$	$C_{22}H_{24}NO_3PS$
Formula weight	349.35	413.45
Temperature [K]	103(2)	100(2)
Wavelength [Å]	1.54184	1.54184
Crystal system	monoclinic	
Space group	$P2_1/c$	$C2/c$
a [Å]	5.6520(2)	36.9730(18)
b [Å]	11.7858(4)	10.3299(5)
c [Å]	26.6778(11)	11.1603(5)
α [°]	90	90
β [°]	92.757(3)	98.588(5)
γ [°]	90	90
Volume [Å^3]	1775.04(11)	4214.6(3)
Z	4	8
Density (calcd.) [Mg m^{-3}]	1.307	1.303
Absorption coefficient [mm^{-1}]	1.479	2.264
F(000)	736	1744
Crystal size [mm^3]	0.30 × 0.03 × 0.01	0.15 × 0.15 × 0.02
θ range for data collection [°]	4.10–75.59	4.45–75.9
Index ranges	$-6 \le h \le 6$, $-14 \le k \le 14$, $-33 \le l \le 31$	$-46 \le h \le 46$, $-12 \le k \le 12$, $-14 \le l \le 12$
Reflections collected	19459	44913
Independent reflections	3563 [R(int) = 0.0290]	4343 [R(int) = 0.0563]
Completeness	98.7% to θ = 67.5°	99.8% to θ = 72.5°
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.84548	1.00000 and 0.76948
Refinement method	full-matrix least-squares on F^2	
Data/restraints/parameters	3563/0/235	4343/0/267
Goodness-of-fit on F^2	1.060	1.058
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0304, $wR2$ = 0.0823	$R1$ = 0.0321, $wR2$ = 0.0857
R indices (all data)	$R1$ = 0.0341, $wR2$ = 0.0851	$R1$ = 0.0376, $wR2$ = 0.0883
Largest diff. peak and hole [e Å^{-3}]	0.269 and –0.261	0.306 and –0.331

Supporting Information (see also the footnote on the first page of this article): Additional experiments and NMR spectroscopic data, ^{1}H and ^{31}P NMR spectra of selected products and ^{13}C NMR spectra of all products, packing figure of **1b** in the crystal.

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