**Supplementary Material for Chemical Communications**


# Novel α-functionally substituted amino acids: diphenylphosphinoglycines

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## Experimental details

All reactions were carried out under dry, oxygen-free argon, using Schlenk techniques and freshly distilled dry solvents. Diphenylphosphine and dicyclohexylphosphine were prepared from the corresponding chlorophosphines by reduction with $LiAlH_4$ in diethylether, other chemicals were purchased. Ethylene (99.5%, Air Liquide) was used without further treatment. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 ($^1$H), 75.5 ($^{13}$C), and 121.5 ($^{31}$P) MHz. Shift references are tetramethylsilane for $^1$H and $^{13}$C and $H_3PO_4$ (85%) for $^{31}$P. Proton or carbon nuclei of phenyl or cyclohexyl groups are denoted *i*, *o*, *m*, *p* and α, β, γ, δ, respectively. Coupling constants refer to $J_{HH}$ in $^1$H and $J_{PC}$ in $^{13}$C NMR data unless stated otherwise. Assignments are supported by DEPT and in part by CH-COSY experiments. Mass spectra were measured on a single-focussing mass spectrometer AMD40 (Intectra). Melting points were determined with a Sanyo Gallenkamp melting point apparatus. TG/DTA was carried out with SETARAM TGDTA 92-16 (5 K/min, under nitrogen atmosphere) and elemental analyses with a CHNS-932 analyser from LECO using standard conditions.

***N-tert*-Butyl-diphenylphosphinoglycine-methanol-solvate (1·MeOH).**
Glyoxylic acid hydrate (939 mg, 10.2 mmol) was dissolved in diethylether (10 mL; ultrasound bath) and added to a solution of diphenylphosphine (1.89 g, 10.2 mmol) and *tert*-butylamine (1.07 mL, 10.2 mmol) in diethylether (20 mL). Precipitation started immediately. After stirring for 24 hthe precipitate was filtered, was washed with diethylether and dried in vacuum. Crystallisation from a small amount of methanol furnished 3.25 g (92%) of **1·MeOH**, mp. 123-125 °C (dec.). **1·MeOH** is air sensitive and starts to decompose above 95 ° C: TG/DTG/DTA (15-250 °C): Δm (95-140 °C) = 22.3% (–MeOH, $–CO_2$ ber. 21.9%) with $Δm_{max.}$ at 120 °C and $Δm_{sh.}$ At 100 and 140 °C, $peak_{exoth.}$ at 114 °C (m), 132 °C (w), $peak_{exoth.}$ at 125 °C (st). $^1$H NMR (d$^8$-THF, CH-COSY, ref. THF δ 1.72): δ 0.96 (s, 9 H, $CMe_3$), 3.26 (s, 3 H, *Me*OH), 4.12 (d, $^2J_{PH}$ = 2.7 Hz, 1 H, CH), 7.20-7.30 (m, 6 H, Ph), 7.50-7.65 (2m, 4 H, Ph). $^{13}$C{$^1$H} NMR (d$^8$-THF, CH-COSY, 135 DEPT): δ 29.4 (C*Me*$_3$), 49.8 (MeOH), 52.5 (d, $^3J_{PC}$ = 9.4 Hz, *C*Me$_3$), 58.3 (d, $^1J_{PC}$ = 12.2 Hz, CH), 128.4 (d,$^3J_{PC}$ = 6.3 Hz, *m*-CH), 128.5 (d,$^3J_{PC}$ = 7.3 Hz, *m*-CH'), 128.9 129.1, *p*-CH'), 134.4 (d, $^2J_{PC}$ = 17.8 Hz, *o*-CH), 135.6 (d, $^2J_{PC}$ = 21.3 Hz, *o*-CH'), 136.9 (d, $^1J_{PC}$ = 16.5 Hz, *i*-C), 138.1 (d, $^1J_{PC}$ = 18.0 Hz, *i*-C'), 176.06 (d, $^2J_{PC}$ = 13.8 Hz, $COO^–$). $^{31}$P{$^1$H} NMR (d$^8$-THF): δ 3.4. Anal. calc. for $C_{18}H_{22}NO_2P·CH_3OH$ (347.40): C, 65.69; H, 7.54; N, 4.03. Found: C, 64.86; H, 7.77; N, 3.95. MS (EI, 70 eV, T = 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).
Storage of the d$^8$-THF solution leads to decomposition, mainly by decarboxylation (δ($^{31}$P) – 15.7).

**Diethylammonium-dicyclohexylphosphonium-bis(glycolate) (2).**
Glyoxylic acid hydrate (345 mg, 3,75 mmol) was dissolved in diethylether (10 mL; ultrasound bath) and added to a solution of dicyclohexylphosphine (0.743 g, 3.75 mmol) and diethylamine (0.39 mL, 3.75 mmol) in diethylether (20 mL). Precipitation started immediately. After stirring for 24 h the precipitate was filtered, was washed with diethylether and dried in vacuum, yield 0.75 g (48%). $^{1}$H NMR ($D_2O$): δ 1.20 (t, $^{3}J$ = 7.3 Hz, 6 H, $CH_3$), 1.15-2.10 (m, 20 H, Cy), 2.50-2.80 (m, 2H, Cy), 2.99 (q, $^{3}J$ = 7.3 Hz, 4 H, $NCH_2$), 5.17 (d, $^{1}J$ = 9.3 Hz, 1 H, $PCH_A$), 5.19 (d, $^{1}J$ = 9.9 Hz, 1 H , $PCH_B$). $^{13}C\{^{1}H\}$ NMR ($D_2O$+$d^8$-THF): δ 12.2 ($CH_3$), 26.8 (C-δ), 27.3-28.1 (m, C-γ, C-β), 31.8 (d, $^{1}J$ = 36.2 Hz, C-α), 32.7 (d, $^{1}J$ = 30.8 Hz, C-α), 43.9, 44.0 ($NCH_2$), 65.9 (d, $^{1}J$ = 33.5 Hz, PCH), 66.5 (d, $^{1}J$ = 33.7 Hz, PCH), 173.6 ($COO^-$).$^{31}P\{^{1}H\}$ NMR ($D_2O$): δ 33.2 (A), 34.0 (B) (diastereoisomer pair A:B ca. 2:1). Anal. calc. for $C_{20}H_{38}NO_6P$ (419.50): C, 57.26; H. 9.13; N, 3.34. Found: C, 57.45; H, 9.23; N, 3.20.

***tert*-Butylammonium-diphenylphosphinoglycolate (3).**
**3** was formed on dissolution of **1·MeOH** in $D_2O$ containing water. $^{1}$H NMR ($D_2O$): δ 1.35 (s, 9 H, $CMe_3$), 3.34 (s, 3 H, *Me*OH), 5.09 (d, $^{2}J_{PH}$ = 3.3 Hz, 1 H, CH), 7.38-7.45 (m, 6 H, Ph), 7.45-7.60 (m, 4 H, Ph). $^{13}C\{^{1}H\}$ NMR ($D_2O$): δ 24.15, 24.20 (2s, C*Me*$_3$), 46.45, 46.47 (2d, $J_{PC}$ = 2.0 Hz, *C*Me$_3$), 50.7 (*Me*OH), 71.1 (d, $^{1}J_{PC}$ = 23 Hz, CHOH), 126.1 (d, $^{3}J_{PC}$ ≈8 Hz, *m*-CH), 126.2 (d, $^{3}J_{PC}$ = 6.3 Hz, *m*-CH'), 126.4, 127.4 (2s, *p*-CH), 130.2 (d, $^{2}J_{PC}$ = 17.1 Hz, *o*-CH), 132.0 (d, $^{2}J_{PC}$ = 19.3 Hz, *o*-CH), 130.7 (d, $^{1}J_{PC}$ = 10.9 Hz, *i*-C), 133.0 (d, $^{1}J_{PC}$ = 11.2 Hz, *i*-C), 175.1 (d, $^{2}J_{PC}$ = 8.0 Hz, COO). $^{31}P\{^{1}H\}$ NMR ($D_2O$): δ = 6.7.

***tert*-Butylammonium-diphenylphosphinoylglycolate (4).**
Aqueous $H_2O_2$ (122 µL, 30%) was added at 0 °C to a solution of **1·MeOH** (379 mg, 1.203 mmol) in water / THF (2:1). After 24 h the solvent was removed in vacuum, the sticky residue was washed with diethylether and dried, yield 350 mg (88%), mp. 177-179 °C. $^{1}$H NMR ($CDCl_3$): δ = 1.18 (s, 9 H, $CMe_3$), 4.79 (d, $^{2}J_{PH}$ = 4.1 Hz, 1 H, CH), 7.34-7.50 (m, 6 H, Ph), 7.80-7.90 (m, 4 H, Ph), 8.2 (vbr, 3 H, OH, $NH_2^+$); $^{1}$H NMR ($D_2O$): δ 1.22 (s, 9 H, $CMe_3$), 4.96 (d, $^{2}J_{PH}$ = 6.1 Hz, 1 H, CH), 7.35-7.45 (m, 4 H, Ph), 7.45-7.53 (m, 2 H, H-*p*), 7.60-7.72 (m, 4 H, Ph). $^{13}C\{^{1}H\}$ NMR ($D_2O$, $d^8$-THF): δ 28.3 (C*Me*$_3$), 53.6 (d, $^{3}J$ = 6.1 Hz, *C*Me$_3$), 73.3 (d, $^{1}J$ = 79.2 Hz, CH), 130.5 (d, $^{3}J$ = 11.7 Hz, 2 *m*-C), 130.8 (d, $^{1}J$ = 100.9 Hz, *i*-C), 133.0 (d, $^{2}J$ = 9.3 Hz, *o*-C), 133.1 (d, $^{2}J$ = 8.9 Hz, *o*-C'), 134.5 (d, $^{4}J$ = 2.2 Hz, *p*-C), 134.6 (d, $^{4}J$ = 2.2 Hz, *p*-C'), 174.3 (COO). $^{31}P\{^{1}H\}$ NMR($CDCl_3$): δ 32.0. Anal. calc. for $C_{18}H_{24}NO_4P$ (349.37): C, 61.88; H, 6.92; N, 4.01. Found: C, 61.43, H, 6.62; N, 4.06.

***N-tert*-Butyl-diphenylthiophosphinoylglycine (5).**
A mixture of sulphur (90.5 mg, 2.83 mmol) and a solution of **1·MeOH** (892.5 mg, 2.57 mmol) in THF (ca. 15mL) was stirred at room temperature for 12-15h. The solvent was removed in vacuum, and the residual white foam was treated with diethylether to give 0.55g (62%) of pure **5**, mp. 109-110 °C (dec.). DTG/DTA (15-250 °C, 5K/min, $N_2$): , $\Delta m_{117°C}$ 12.7% (–$CO_2$), max.$_{exoth.}$ 116-117 (st), max.$_{endoth.}$ 118-120 (st) °C. **5** is insoluble in $D_2O$, soluble in methanol, in $CDCl_3$ and in THF. $^{1}$H NMR($CDCl_3$): δ 1.28 (s, 9 H, $CMe_3$), 4.08 (d, $^{2}J_{PH}$ = 10.7 Hz, 1 H, CH), 7.35-7.73 (m, 8 H, Ph), 8.52 (m, $^{3}J_{PH}$ = 13.6, 2 H, Ph). $^{13}C\{^{1}H\}$ NMR($CDCl_3$): δ 27.2 (C*Me*$_3$), 57.3 (d, $^{3}J_{PC}$ = 3.4 Hz, *C*Me$_3$), 57.5 (d, $^{1}J_{PC}$ = 39.7 Hz, CH), 128.4 (d,$^{3}J_{PC}$ = 13.4 Hz, *m*-CH), 128.6 (d, $^{1}J_{PC}$ = 87.5 Hz, *i*-C), 129.0 (d,$^{3}J_{PC}$ = 13.2 Hz, *m*-CH'), 129.2 (d, $^{1}J_{PC}$ = 85.2 Hz, *i*-C'), 132.1 (d, $^{2}J_{PC}$ = 11.3 Hz, *o*-CH), 132.5 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-CH), 132.8 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-CH'), 133.0 (d, $^{2}J_{PC}$ = 10.9 Hz, *o*-CH'), 164.8 (s, $COO^-$). $^{31}P\{^{1}H\}$ NMR($CDCl_3$): δ 51.5. Anal. calc. 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%.

In $CDCl_3$ and in THF solution slow decarboxylation occurs: 50-60% of **5** were converted to $Ph_2P(S)CH_2NHtBu$ within 6 days at room temperature.

**Ethylene oligomerisation**

The technical equipment and details of the ethylene oligomerisation used here are the same as reported in J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim, G. Fink, *Chem. Eur. J*. **2003**, *9*, 6093-6107.

a) A solution of **1·MeOH** (38 mg, 110 μmol) in THF (10 mL) was added at 0 °C to a solution of $Ni(COD)_2$ (34 mg, 124 μmol) in THF (10 mL). The mixture was stirred for 10 min at 0 °C and 30 min. at 20 °C (colour change to orange) and then added to the autoclave. The autoclave (75 mL, stainless steel) was pressurised with ethylene ($p_{start}$ 30 bar, 8.1 g $C_2H_4$), closed, set in the preheated bath (100 °C) and heated for 15 h at 100 °C. After cooling and weight control unconverted ethylene was released through a cooling trap (conversion 85 %, TON 2230). THF and volatiles were flash distilled (1.5 Torr, bath up to 150 °C). The residue was stirred for 1 d with methanol / conc. hydrochloric acid (1:1), washed with water followed by methanol and then dried to give 5.2 g waxy polyethylene. $^1$H NMR (in $C_6D_5Br$ at 100 °C after swelling for 1 d at 120 °C under argon, acquisition time 4.9-5.4 s, delay 1.0 s, reference *p*-C<u>H</u> of the solvent δ = 7.23): α/internal olefins 93:7:%, methyl/olefin 1.5, average molar mass by $^1$H NMR integration (similar to $M_n$) 1230 g·mol$^{-1}$, after extraction of oligomers with $CH_2Cl_2$ (10 mL) mp. 113-117 °C, d = 0.958 g·cm$^{-3}$.

b) The experiment was performed as described in a) except use of toluene instead of THF and a higher initial pressure ($p_{start}$ 50 bar, 14.4 g $C_2H_4$): conversion 12.7 g, 88 %, TON 4530, waxy polyethylene, $^1$H NMR (in $C_6D_5Br$ as above): α/internal olefins 90:10:%, methyl/olefin 1.3, average molar mass 900 g·mol$^{-1}$, mp. 115-118 °C (around the stirrer 120-123 °C), d = 0.933 g·cm$^{-3}$. In this experiment the pressure-time plot was registered and shows the oligomerisation start after ca. 30 min. (thereof ca. 20 min. necessary to reach $T_{intern}$ ca. 100 °C in the autoclave) and consumption of ca. 50% of $C_2H_4$ within one hour reaction time.