Polyhedron 117 (2016) 795–802

Contents lists available at ScienceDirect

Polyhedron

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

α-Phosphanyl amino acids: Diphenylphosphanyl glycines with a chiral *N*-substituent

Joanna Lach [a], Normen Peulecke [a,1], Peter G. Jones [b], Ina Dix [c,2], Joachim W. Heinicke [a,*]

[a] Institut für Biochemie, Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Str. 4, D-17489 Greifswald, Germany
[b] Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany
[c] Institut für Anorganische Chemie, Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany

ARTICLE INFO

Article history:
Received 29 March 2016
Accepted 10 July 2016
Available online 15 July 2016

Keywords:
Phosphorus
Chiral N-substituent
Amino acids
Multicomponent reactions
Transition metal catalysts

ABSTRACT

The first α-phosphanyl amino acetic acids (phosphanyl glycines) with a chiral *N*-substituent **1a**–**g** have been synthesized by one-pot three-component condensation of diphenylphosphane and enantiomerically pure primary amines of the type (*L*)- or (*R*)-$R^1R^2CHNH_2$ with glyoxylic acid monohydrate in diethyl ether at room temperature. Crystals of the *N*-(1*S*)-phenylethyl derivative **1d**·MeOH, grown from methanol, contained only the (1*S*,α*S*)-diastereoisomer. In [d_8]THF or CD_3OD solution, however, two diastereoisomers were always observed for **1a**–**g**, usually in a diastereoisomeric ratio in the range 67:33% to 80:20%. This, together with the general sensitivity of the phosphanylglycines to hydrolysis, H-D exchange at the acidic α-CH and facile air oxidation in CD_3OD solution and decarboxylation on heating in aprotic solvents are serious shortcomings and militate against the use as ligands, e.g. in Rh- or Ir-catalyzed asymmetric hydrogenations. Nickel catalysts, generated in situ with $Ni(COD)_2$ in THF and/or 1-hexene, proved however more stable and allowed selective oligomerization of ethylene at 100 °C, probably by formation of a stabilizing P—C—C(O)O^- hybrid ligand in the catalyst backbone. Complexes and catalysts of this type might thus offer chances for use of this facile available asymmetric ligands.

1. Introduction

Enantiomerically pure ("enantiopure") phosphanes have proved to be versatile ligands in a variety of enantioselective homogenous transition-metal-catalyzed organic transformations [1]. A frequently used synthetic strategy is to generate such ligands by introduction of a phosphanyl group into asymmetric precursor compounds. Early reports on combinations of secondary phosphanes with natural L-amino acids used a Mannich-type condensation with formaldehyde [2], yielding enantiopure *N*-phosphanylmethyl amino acids [3]. Later these studies were extended to primary phosphanes, which with paraformaldehyde and glycine or other amino acids led to six-membered 1,3,5-diazaphosphorinane [4] and a variety of eight-membered 1,5,3,7-diazadiphosphacyclooctane derivatives [5]. *N*-Phosphanyl-substituted amino acid esters were prepared by direct reaction with diphenylchlorophosphane [6]. The first sulfur-protected phosphanyl amino acid derivatives with phosphorus in β- to ε-position to the center of asymmetry were synthesized about twenty years ago by various methods [7,8] and were investigated with respect to their suitability for generation of synthetic peptide libraries, their phosphane complexes with late transition metals and the catalytic applications of these complexes. Use of the phosphanyl peptide catalysts led to moderate ee's in various asymmetric organic syntheses [7,8]. To find out whether α-phosphanyl glycine ligands with chiral *N*-substituent might be isolable in enantiopure form, usable in transition-metal-catalyzed reactions and capable of inducing enantioselectivity, we employed our recently reported facile one-pot three-component synthesis of *N*-monosubstituted α-phosphanyl glycines [9] with a variety of commercially available asymmetric primary amines and tested a crystallographically characterized phosphanyl amino acid with 1*S*,α*S*-configuration for use as a ligand in Ni-catalyzed ethylene oligomerization and in selected asymmetric Rh- and Ir-catalyzed hydrogenations. We report here on the first phosphanyl glycines with chiral substituent at nitrogen, their structural properties and the results of the catalytic tests.

* Corresponding author.
E-mail address: heinicke@uni-greifswald.de (J.W. Heinicke).
[1] Current address: Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29 A, 18059 Rostock, Germany.
[2] Current address: Novartis Pharma AG, CH-4056 Basel, Switzerland.

http://dx.doi.org/10.1016/j.poly.2016.07.011
0277-5387/

2. Results and discussion

2.1. Synthesis

A number of commercially available enantiopure primary amines with a stereogenic carbon atom in α-position to nitrogen were mixed with one equivalent of diphenylphosphane and then converted with glyoxylic acid monohydrate (GAH) in ethereal solution at room temperature. In order to achieve reproducible results, complete dissolution of GAH is required before combining its solution with the ethereal solution of the amine and phosphane. To accelerate the rather slow dissolution and suppress self-condensation reactions of GAH, [10] dilute solutions (ca. 0.5 g GAH in 15–20 mL) were prepared in an ultrasound bath at room temperature. After mixing with the solution of amine and phosphane, a primary precipitate was usually formed, which for some amines redissolved and after some hours formed a secondary precipitate, or converted without perceptible dissolution to a crude product, after crystallization from methanol identified as the corresponding phosphanyl amino acetic acid **1a–g** (henceforth termed *phosphanyl glycines*). For some amines, however, no precipitation was observed. In these cases ether and water, liberated in the condensation reaction, were removed under vacuum as far as possible. The crude products were all very soluble in methanol and formed methanol solvates **1a–g**·*x*MeOH ($x = 0.6$ for **1e**, otherwise $x = 1$); these were less soluble and crystallized or precipitated from the solution (Scheme 1). Attempts at recrystallization from hot methanol led to partial decomposition; such problems were avoided by the use of a sufficiently large excess of dry methanol for complete dissolution of the crude product at room temperature and concentration under vacuum, if necessary, for isolation.

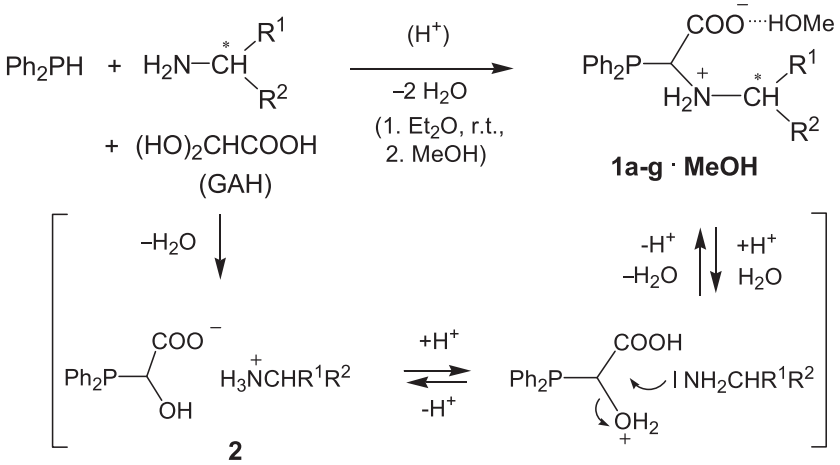
Concerning the mechanisms, the primary and secondary precipitates in ether are probably transient organoammonium glyoxylates and phosphanyl glycolates **2**, respectively, which slowly convert to **1a-g**, at the latest during crystallization from methanol. Compounds of type **2** have been detected as intermediates in analogous reactions with *tert*-butylamine, 1-adamantylamine or some primary *N*-arylamines to the corresponding *N*-monosubstituted phosphanyl glycines and as equilibrium species in reactions of the latter with small amounts of water [9], whereas *N*-secondary and tertiary organoammonium phosphanyl glycolates are isolable and have been characterized by NMR data and crystal structure analysis [11].

2.2. Structure elucidation and chemical properties

Small single (but twinned) crystals of **1d**·MeOH were studied by X-ray diffraction using Cu Kα-radiation. The compound crystallizes in the monoclinic space group $P2_1$, and contains two zwitterionic molecules and two methanol molecules in the asymmetric unit. The two molecules of **1d** are closely similar, both possessing (1*S*, α*S*)-configuration at the asymmetric carbon sites (Fig. 1), but differing slightly in ring orientations and particularly in the orientation of the methoxy group. The planes of phenyl ring 2 and the carboxylate group are arranged nearly perpendicularly to the P1—C1 axis [C1—P1—C21—C22 90.8(3), 90.4(3)°; P1—C1—C2—O1 −89.4(3), −87.3(3)°] whereas the plane of phenyl ring 3 at phosphorus is rotated by about 60° from the same axis [C1—P1—C31—C32 −29.8 (4), −38.1(3)°] in a propeller-like arrangement.

Both molecules pack via translational symmetry to form separate chains parallel to the short *x* axis; hydrogen bonds $NH\cdots OC_{carboxylate}$ connect adjacent molecules, and the corresponding graph set is *C*(5). The methanol molecules are attached to the chains via hydrogen bonds $NH\cdots OH_{methanol}\cdots OC_{carboxylate}$, forming rings of graph set $R_3^3(8)$. The packing, depicted in Fig. 2, shows two chains of the molecules 1 (arbitrarily numbered) in the region $z = ½$ and two chains of the molecules 2 in the region $z = 0$ and 1.

The CP-MAS ^{31}P NMR spectra of **1d**·MeOH confirmed the phosphanyl glycine nature of the product. The phosphorus resonance appeared at −8.8 ppm, about 9 ppm upfield from the solution ^{31}P NMR signal of solvated **1d**, while the CP-MAS ^{13}C NMR spectrum clearly proved the P—CH—N structure by superimposed P—*CH*—N and N—*CH*(Me)aryl signals around 62 (broad sh) and 60 (br) ppm. We detected no signal that would indicate the P—CH—O structure of the assumed intermediate, which should appear at 70–75 ppm (see below). The signal widths however prevented a decision as to whether one or two diastereoisomers of **1d**·MeOH were present.



1	a	b	c	d	e	f	g
R^1 :	Me	Me	Me	Me	Et	Me	Me
R^2 :	*i*Pr	Ph	Ph	*p*-C_6H_4OMe	Ph	1-Naph	2-Naph
C^*H :	(*S*)	(*R*)	(*S*)	(*S*)	(*R*)	(*R*)	(*S*)

Scheme 1. Three-component synthesis of methanol solvates of phosphanyl glycines **1a–g** with chiral *N*-substituent, and hydrolytic equilibrium in solution between **1** and **2**.

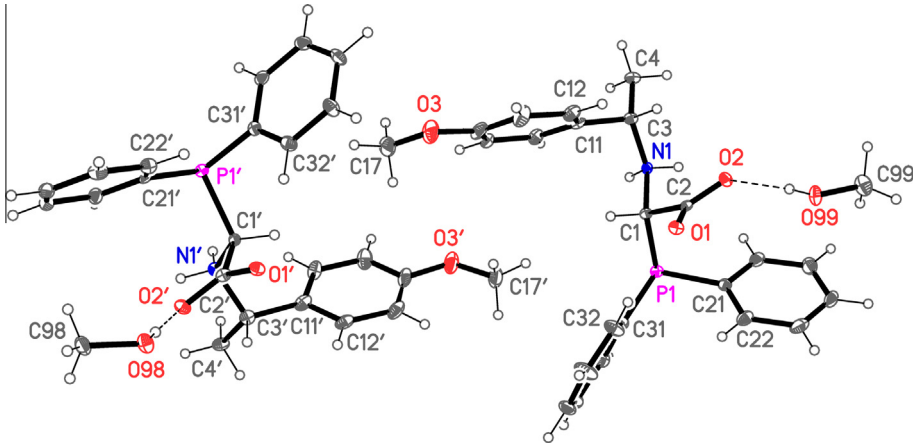


Fig. 1. Molecular structure of **1d**·MeOH in the crystal (ellipsoids with 30% probability). Selected bond lengths (Å) and angles (°) of molecule 1: P(1)—C(1) 1.896(3), P(1)—C(21) 1.842(4), P(1)—C(31) 1.845(4), N(1)—C(1) 1.505(4), N(1)—C(3) 1.510(4), C(1)—C(2) 1.534(5); C(1)—P(1)—C(21) 101.19(15), C(1)—P(1)—C(31) 102.76(16), C(21)—P(1)—C(31) 104.41(17), N(1)—C(1)—C(2) 108.9(3), N(1)—C(1)—P(1) 107.4(2), C(2)—C(1)—P(1) 115.0(2), O(2)—C(2)—O(1) 127.2(3); C(1)—P(1)—C(21)—C(22) 90.8(3), C(1)—P(1)—C(31)—C(32) −29.8(4), N(1)—C(3)—C(11)—C(12) 119.8(4), P(1)—C(1)—C(2)—O(1) −89.4(3). Values for molecule 2 (atom names with primes) may be obtained from the deposited material.

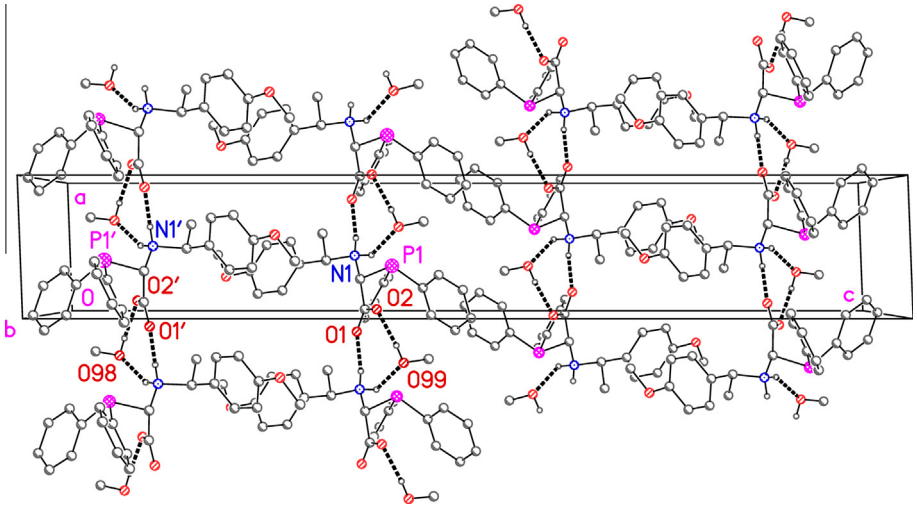


Fig. 2. Packing of **1d**·MeOH in the crystal. The shortest hydrogen bonds (D—H···A, d(D—H) d(H···A), d(D···A), <(DHA)) are N(1′)—H(02′)···O(1′)#1 [0.88(2), 1.81(2), 2.695(4), 176(4)], N(1)—H(02)···O(1)#1 [0.89(2), 1.85(3), 2.714(4), 166(4)], O(99)—H(099)···O(2) [0.83(4), 1.89(4), 2.713(4), 172(5)], and O(98)—H(098)···O(2′) [0.83(4), 1.89(4), 2.722 (4), 175(5)]. The symmetry operator #1 is an *x* axis translation.

The solution NMR spectra of this compound in [d_8]THF or CD_3OD always displayed two sets of signals, which represent two diastereoisomers A and B in a molar ratio of 75:25% to 80:20%. Similarly, for all the other phosphanyl glycine methanol solvates two diastereoisomers were observed in solution by NMR spectroscopy. The molar ratio varied from ca. 5:4 for **1a**·MeOH and ca. 2:1 for **1c**·MeOH and **1g**·MeOH to ca. 3:1 to 4:1 for **1b**·MeOH, **1e**·0.6 MeOH and **1f**·MeOH. The P—CH—N nature of both solution isomers followed from characteristic upfield shifts of the ^{13}C NMR doublets (δ = 58.0–61.2 ppm, $^{1}J_{PC}$ = 13.6–19.7 Hz) compared to P—C—O ^{13}C doublet signals observed in organoammonium phosphanyl glycolates (δ = 71.1–75.7 ppm, $^{1}J_{PC}$ = 23–26 Hz, [9,11]). Interestingly, the ^{31}P resonances of **1d**·MeOH and the other phosphanyl glycines also appear somewhat upfield (δ = −0.6–1.0 ppm) from the signal range of the organoammonium phosphanyl glycolates (δ = 4–8 ppm, [9,11]) and thus allow an easy distinction between the two types of compounds. Complete assignments of all other significant ^{13}C and proton signals on the basis of typical shift ranges, coupling constants and intensity ratios allowed unambiguous structure elucidation. The formation of a second diastereoisomer may be attributed to the kinetic lability of phosphanyl glycines [9], leading to a solution equilibrium of diastereoisomers, controlled by the relative thermodynamic stability of the solvated molecules. During crystal growing, matrix effects may favor crystallization of only that diastereoisomer which under the given conditions leads to the more stable crystal structure, as shown for the crystal of **1d**·MeOH analysed by XRD; no other types of crystal were discovered for **1d**·MeOH, but an exhaustive search was not conducted. Whether single crystals of the other phosphanyl glycines with chiral N-substituent can accommodate only one enantiomer or both diastereoisomers would require further crystal structure studies. The low kinetic stability and dominance of one of the two diastereoisomers in solution suggest, however, that during crystallization only that diastereoisomer yielding the more stable crystal structure will be incorporated.

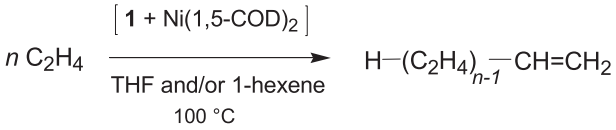
Apart from the isomerization, slow decarboxylation was also observed for all of the above-mentioned phosphanyl glycines in [d_8]THF solution at room temperature during prolonged NMR measurements or after storage of NMR samples (2–6 d). This was

indicated by ^{31}P NMR trace signals at $\delta = -19$ ppm (compound type Ph_2PCH_2NHR, *cf.* [9a]) and sometimes by an additional smaller trace signal at $\delta = -27$ ppm (compound type $(Ph_2PCH_2)_2NR$, *cf.* [12]). The decarboxylation becomes more extensive on heating and is fast in refluxing THF or $CDCl_3$ or on heating without solvent at ca. 100 °C. This decomposition is attributable to intramolecular protonation of the phosphorus atom and has been studied mechanistically in detail for diphenylphosphanyl acetic acid [13]. Small signals of Ph_2PH (δ ^{31}P = −40 ppm) in the solution spectra of **1a**–**g**·MeOH indicate solvolysis equilibria, with replacement of the Ph_2P-substituent by the methoxy group of methanol, and were strongest in the case of **1a**·MeOH (in [d_8]THF at 25 °C ca. 10% by ^{31}P integration). Residual water from the condensation reaction would lead preferably to signals of **2**, as shown in the case of **1b**·MeOH by addition of water to the NMR sample (**2b**, δ ^{31}P = 6.8 ppm) and observed in studies of hydrolysis equilibria of *N*-aryl- and *N*-alkyl diphenylphosphanyl glycines [9]. In CD_3OD solution at room temperature decarboxylation was suppressed or very slow, while H-D exchange of the acidic proton at the α-carbon atom led to low intensity or disappearance of the α-CH signals. The aforementioned partial replacement of the Ph_2P group by CH_3O and CD_3O-substituents and formation of equilibrium amounts of Ph_2PH and Ph_2PD may be responsible for the increased sensitivity to air oxidation. Thus, storage or prolonged NMR measurements of CD_3OD solutions of **1b**·MeOH in tubes, closed with plastic caps that obviously allowed slow diffusion of air, led to ^{31}P NMR signals for a variety of oxidation products (δ range 26–35 ppm), which were not further studied.

2.3. Catalytic tests

The kinetic lability of the phosphanyl glycines is a serious drawback for coordination chemical and catalytic studies. Tests of **1d**·MeOH as ligand precursor in Rh- and Ir-catalyzed hydrogenations of various substituted acrylic acid ester derivatives using 1 mol% $[Rh(COD)_2]BF_4$ or $[Ir(COD)Cl]_2$ and ligand/metal ratios of 2:1 and 1:1 in CH_2Cl_2 or methanol solution were not successful and led at a pressure of 2.5 bar hydrogen at 24 h/25 °C to very low (acetamidoacrylic acid methylester) or insufficient hydrogenation (2-methylene-succinic acid dimethylester, (*E*)-methyl-3-acetamidbut-2-enoate, 6–28%) without any enantioselectivity.

However, the use of suitable phosphanyl glycines for transition metal catalysts with P^O$^-$ hybrid ligands as backbones to stabilize the active site may have a better chance of success. This has been shown for suitable *N*-aryl or sufficiently bulky *N*-alkyl phosphanyl glycines by the generation of nickel catalysts for the oligomerization of ethylene, and inspired us to conduct further catalytic tests. **1b**·MeOH and **1d**·MeOH were found to form precatalysts with Ni$(COD)_2$ in THF; these were activated and converted ethylene under pressure at ca. 100 °C selectively to linear olefins, mainly with vinyl and methyl end groups (Scheme 2, Table 1, entries 1 and 2). In the presence of 1-hexene, the ethylene conversion was slower (Fig. 3) because of competition of ethylene and hexene for coordination at nickel, but the insertion into the growing chain remained selective for C2. 1-Hexene was not incorporated into the chains, as shown by the NMR spectra of the waxy oligomers (Table 1, entries 3 and 4). The average chain lengths became greater for a lower content of the O-donor solvent, which also competes for coordination at



Scheme 2. Ethylene oligomerization by catalysts, generated in situ from phosphanyl glycines and Ni$(COD)_2$, molar ratio 1:1, in THF, THF/1-hexene or 1-hexene.

Table 1
Screening of **1b**·MeOH and **1d**·MeOH in Ni-catalyzed oligomerizations of C_2H_4.

Entry	Catalyst;[a] C_2H_4 g (mmol); solvents (mL)	Conversion (%), TON (mol/mol·h)	Wax (g); liquid: C4, C6, C8 etc.[b] (%)	Wax	
				M.p. (°C), D[c] (g/cm^3)	M [g/mol], Vin/CH=CH[d]
1	**1b**/Ni; 12.8 (456); THF (20)	88, 3357	10; 18, 31, 26, 16, 6, 3	117–119; 0.94	1054, 93:7
2	**1d**/Ni; 11.2 (314); THF (20)	95, 3821	2.0; 51, 38, 8, 3	100; 0.90	370, 85:15
3	**1d**/Ni; 11.5 (322); 1-hexene (10), THF (10)	77, 3143;	8.2; n.d.	105; 0.89	910, 80:20
4	**1d**/Ni; 11.9 (333); 1-hexene (20)	87, 3679	8.8; 17, 39, 25, 19	112; 0.91	1550, 74:26

[a] Catalyst prepared from solutions of **1b**·MeOH (120 μmol) or **1d**·MeOH (100 μmol) and equimolar amounts of Ni$(COD)_2$ in THF, stirring the mixture for ca. 15 min at 0–10 °C, transfer to autoclave, pressurizing with ethylene to 40–50 bar and heating to 100 °C for ca. 15 h.
[b] Estimated composition of volatile oligomers in the flash distillate by GC; C4 partly lost.
[c] Density of PE wax estimated from tablets, pressed at ca. 10 kbar.
[d] M_{NMR} and Vin/CH=CH ratio estimated by ^{1}H NMR integration of CH_2 and CH_3 signals versus vinyl and CH=CH signals; measurement after 1 d swelling at 100 °C in C_6D_5Br.

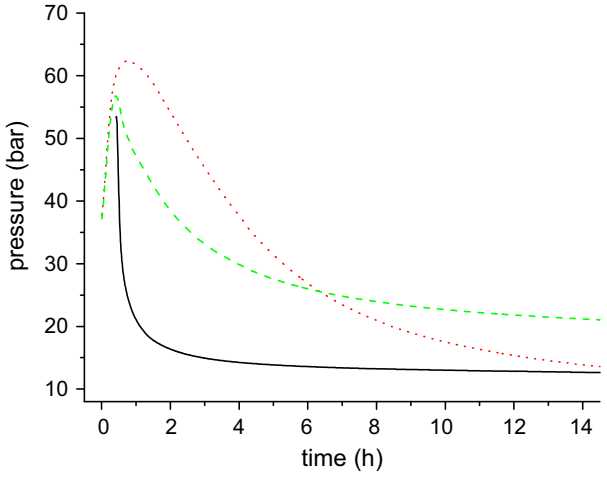


Fig. 3. Pressure-time plots of ethylene oligomerization catalyzed by **1d**·MeOH/Ni$(COD)_2$ in (a) THF (solid line), (b) in THF/1-hexene (1:1) (dashed line) and c) in 1-hexene (dotted line). The plot for the ethylene consumption by catalysis with **1b**·MeOH/Ni$(COD)_2$ in THF is similar to that in Fig. 3a.

nickel. Addition of styrene blocked the catalyst. The high selectivity for formation of linear α-olefins suggest a similar oligomerization mechanisms to that proposed for nickel catalysts generated with diphenylphosphanyl acetic acid [14]. The α-branched *N*-substituent seems to be sufficient bulky to hinder or prevent interfering interactions of the amino group with the catalyst metal. The maintenance of the catalytic activity at ca. 100 °C is remarkable, and contrasts with the quite rapid thermal decomposition of uncoordinated diphenylphosphanyl acetic acid or its amino derivatives **1** at this temperature. This hints at higher thermal stability of the metal-coordinated P—C—COO$^-$-ligands.

3. Conclusions

Enantiopure primary amines undergo a one-pot three-component condensation with secondary diarylphosphanes and glyoxylic acid hydrate in solvents such as diethyl ether. After separation

from moist ether and crystallization from methanol phosphanyl glycine methanol solvates were obtained. As shown for **1d**·MeOH, the crystals may consist of only one enantiomer, while solution NMR spectra detect equilibrium amounts of two diastereoisomers. The kinetic lability of the phosphanyl glycines in solution prevented separation of the diastereoisomers and limits applications in transition metal complex chemistry and catalysis. The reaction with $Ni(COD)_2$ to nickel precatalysts, which by heating with ethylene under pressure lead to formation of efficient oligomerization catalysts, shows however that the phosphanyl glycines may form transition metal compounds that are sufficiently stable to act as catalysts. The same high selectivity for oligomerization of ethylene to linear α-olefins as observed for (organo)nickel phosphanyl acetate catalysts, even in the presence of excess 1-hexene, suggest formation of organonickel(II) P^COO^--chelate complexes and that other types of (organo)transition metal P^COO^--chelate complexes might also be accessible from the new ligands by suitable methods and perhaps be usable as catalysts.

4. Experimental

4.1. General remarks

All manipulations were carried out under nitrogen atmosphere using Schlenk techniques. The solvents were dried by standard methods and freshly distilled before use. Diphenylphosphane was synthesized from triphenylphosphane by cleavage of a phenyl group with two equivalents of sodium in liquid ammonia and neutralization with dry NH_4Cl [15]. Other chemicals were purchased and used without further treatment. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 or Avance300 (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. For longer NMR measurements, tubes should be sealed by melting or closed by glass stoppers to prevent oxidation by air, which slowly diffuses through commercial plastic caps. Chemical shifts δ are given in ppm and referred to tetramethylsilane for ^1H and ^{13}C and H_3PO_4 (85%) for ^{31}P or to solvent signals calibrated with these references. Coupling constants refer to J_{HH} in ^1H NMR and to J_{PC} in ^{13}C NMR data unless stated otherwise. Assignments of the P-phenyl signals (two sets for each diastereoisomer) are indicated by *i*, *o*, *m*, *p*, by A and B for different diastereoisomers (if distinguishable) and by an additional apostrophe (') for phenyl signals of the *N*-substituent. The assignments are tentative and based on characteristic shift ranges, coupling constants and intensity ratios, for **1d**·MeOH additionally supported by HH- and CH-COSY experiments. ^{31}P integrals, referring to AQ 0.33 s and D1 2.0 s, are not quantitative but comparable for closely related substances with similar relaxation times. ESI-HRMS spectra of **1d** were recorded with a high-resolution mass spectrometer APEX IV (Bruker Daltonik). Because of the isomerization in solution the specific rotation ([α]) of polarized light was not given for the new asymmetric compounds. Melting points (uncorrected) were determined with a Sanyo Gallenkamp melting point apparatus, elemental analysis with a CHNS-932 analyzer from LECO using standard conditions.

4.2. [(1S)-(1,2-Dimethyl-propylamino)]-diphenylphosphanyl-acetic acid methanol solvate (*1a*·MeOH)

A solution of Ph_2PH (1.01 g, 5.42 mmol) and (2*S*)(+)-2-amino-3-methylbutane (0.47 g, 5.45 mmol) in diethyl ether (10 mL) was added at room temperature (ca. 22 °C) to a solution of glyoxylic acid hydrate (0.50 g, 5.43 mmol) in diethyl ether (20 mL), freshly prepared in an ultrasound bath. After few minutes a precipitate was observed. Stirring was continued overnight, the precipitate separated, washed with ether and dried in vacuum to give 0.90 g (50%) of a white powder. Crystallization from methanol afforded small colorless crystals of **1a**·MeOH. Anal. Calc. for $C_{19}H_{24}NO_3P{\cdot}CH_3OH$ (361.41): C, 66.46; H, 7.81; N, 3.88; found: C, 66.46; H, 7.91; N, 3.86%. The solution NMR spectra in [d_8]THF displayed two diastereoisomers (A, B) and minor amounts of Ph_2PH by partial solvolysis (molar ratio after 4–6 h ca. 50:38:12, after 1 d ca. 37:33:30 by integration of *o*-CH ^{13}C NMR signals). ^1H NMR ([d_8]THF): δ = 0.74 (d, ^3J = 6.8 Hz, 3H, Me_B), 0.78 (d, ^3J = 7.0 Hz, 3H, Me_B), 0.81 (d, ^3J = 6.8 Hz, 6H, $2Me_{AB}$), 0.87 (d, ^3J = 6.5 Hz, 3H, Me_A), 0.90 (d, ^3J = 6.4 Hz, 3H, Me_A), 1.16–1.74 (m, 2H, $2CH_{AB}$), 2.43–2.55 (m, 2H, $2NCH_{AB}$), 4.14 (d, $^2J_{PH}$ = 2.5 or 4.5 Hz, 1H, PCH_B), 4.15 (d, $^2J_{PH}$ = 3.2 or 5.4 Hz, 1H, PCH_A), 5.70 (v br s, 3H, NH, OH), 7.21–7.34 (m, 6H, Ph), 7.40–7.67 (m, 4H, Ph); 3.26 (s, 3H, *Me*OH) ppm. $^{13}C\{^1H\}$ NMR and DEPT-135 ([d_8]THF): δ = 15.46, 16.20, 16.96, 17.93, 18.91, 19.49 (6 CH_3), 32.03 (CH_B), 34.27 (CH_A), 58.01 (d, ^3J = 7.9 Hz, NCH_B), 59.36 (d, ^3J = 8.4 Hz, NCH_A), 60.53 (d, ^1J = 15.1 Hz, PCH_B), 62.09 (d, ^1J = 14.1 Hz, PCH_A), 128.49 (d, ^3J = 5.1 Hz, *m*-CH), 128.55 (d, ^3J = 4.1 Hz, *m*-CH), 128.61 (d, ^3J = 4.3 Hz, *m*-CH), 128.70 (d, ^3J = 5.4 Hz, *m*-CH), 128.96, 129.09, 129.68, 129.88 (4 *p*-CH_{AB}), 133.86 (d, ^2J = 17.5 Hz, *o*-CH_A), 134.10 (d, ^2J = 18.6 Hz, *o*-CH_B), 135.21 (d, ^2J = 21.1 Hz, *o*-CH), 135.44 (d, ^2J = 21.1 Hz, *o*-CH), 136.96 (br d, ^1J = 14.6 Hz, *i*-C_q), 137.85 (br d, ^1J = 18.2 Hz, *i*-C_q), 174.09 (d, ^2J = 9.4 Hz, COO^-), 174.84 (br, COO^-); 49.77 (s, *Me*OH) ppm; $^{31}P\{^1H\}$ NMR ([d_8]THF): δ = 0.3, 0.7 (A, B) (integral ratio 45:55) ppm.

4.3. Diphenylphosphanyl-[(1R)-(1-phenyl-ethylamino)]-acetic acid methanol solvate (*1b*·MeOH)

A freshly prepared solution of glyoxylic acid hydrate (534 mg, 5.8 mmol) in diethyl ether (20 mL) was added at room temperature to a solution of diphenylphosphane (1.08 g, 5.8 mmol) and *R*(+)-methylbenzylamine (0.74 mL, 5.8 mmol) in diethyl ether (10 mL). The solution was stirred overnight and separated from a small amount of a sticky precipitate. The solvent was removed in vacuum and methanol added (>20 mL). The solid residue dissolved immediately, but shortly afterwards the methanol solvate of **1b** started to crystallize, forming a thick precipitate. It is much less soluble in cold methanol than the primary product and insoluble in Et_2O. Crystallization from slightly warmed methanol (max. 30 °C), washing with diethyl ether and drying under vacuum provided 1.5 g (65%) of colorless needles, mp. (dec.) 104–105 °C. Anal. Calc. for $C_{22}H_{22}NO_2P{\cdot}CH_3OH$ (395.43): C, 69.86; H, 6.63; N, 3.54; found: C, 69.93; H, 6.71; N, 3.67%. The solution NMR spectra in [d_8]THF revealed two diastereoisomers A and B, molar ratio 75:25% by integration of proton NMR signals. ^1H NMR ([d_8]THF): δ = 1.24 (d, ^3J = 6.5 Hz, 3H, Me_A), 1.25 (d, ^3J = 6.6 Hz, 3H, Me_B), 3.71 (br q, ^3J = 6.7 Hz, $2NCH_{AB}$), 3.77 (d, $^2J_{PH}$ = 3.2 Hz, 1H, PCH_A), 4.20 (d, $^2J_{PH}$ = 1.2 Hz, 1H, PCH_B), 4.5–6.0 (v br, 3H, NH, OH), 7.12–7.43, 7.50–7.60 (m, 15H, 3 Ph); 3.26 (3H, *Me*OH) ppm. $^{13}C\{^1H\}$ NMR and DEPT-135 ([d_8]THF): δ = 22.76 (Me_B), 24.91 (Me_A), 57.80 (d, ^3J = 9.1 Hz, NCH_B), 58.63 (d, ^3J = 9.6 Hz, NCH_A), 60.71 (d, ^1J = 14.2 Hz, PCH_A), 60.93 (d, ^1J = 19.7 Hz, PCH_B), 127.38 (*p*′-CH_A), 127.53 (*p*′-CH_B), 127.68 (2*o*′-CH_B), 128.28 (2*o*′-CH_A), 128.59 (d, ^3J = 6.7 Hz, 4 *m*-CH_A), 128.63, 128.77 (br, superimp. sh, 2*m*′-CH_{AB}, 2*m*-CH_B), 128.82 (d, ^3J = 7.7 Hz, 2*m*-CH_B), 129.04 (*p*-CH_B), 129.14 (*p*-CH_A), 129.69 (*p*-CH_A), 129.78 (*p*-CH_B), 133.92 (d, ^2J = 18.5 Hz, 2*o*-CH_B), 134.08 (d, ^2J = 18.7 Hz, 2*o*-CH_A), 135.17 (d, ^2J = 21.2 Hz, 2*o*-CH_A), 135.38 (d, ^2J = 20.9 Hz, 2*o*-CH_B), 136.48 (d, ^1J = 18 Hz, *i*-C_A), 137.08 (d, ^1J = 17.2 Hz, *i*-C_A), ca. 137.7 (d, noise level, 2*i*-C_B), 145.16 (*i*′-C_A), 146.60 (*i*′-C_B), ca. 173.2 (d, noise level, COO_B), 173.84 (d, ^2J = 12.0 Hz, COO_A); 49.76 (MeOH) ppm. $^{31}P\{^1H\}$ NMR ([d_8]THF): δ = 1.0, 0.3 (A, B, integral ratio 73:27) ppm.

4.4. Diphenylphosphanyl-[(1S)-(1-phenyl-ethylamino)]-acetic acid methanol solvate (**1c**·MeOH)

Reaction of glyoxylic acid hydrate (300 mg, 3.26 mmol), diphenylphosphane (600 mg, 3.22 mmol) and *S*(−)-methylbenzylamine (390 mg, 3.22 mmol) in ethereal solution (15+5 mL) and workup as described for **1b**·MeOH gave 800 mg (63%) white powder, mp. (dec.) 97–103 °C. Anal. Calc. for $C_{22}H_{22}NO_2P{\cdot}CH_3OH$ (395.43): C, 69.86; H, 6.63; N, 3.54; found: 69.88; H, 6.53; N, 3.62%. The solution NMR spectra in [d_8]THF showed two diastereoisomers A and B, molar ratio 67:33% (by integration of proton NMR signals. ^{1}H NMR ([d_8]THF): δ = 1.24 (d, ^3J = 6.5 Hz, 3H, Me_A), 1.25 (d, ^3J = 6.5 Hz, 3H, Me_B), 2.30–3.15 (s br, 3H, NH, OH), 3.70 (br q, ^3J = 6.5 Hz, 2H, NCH_{AB}), 3.76 (d, $^2J_{PH}$ = 3.2 Hz, 1H, PCH_A), 4.19 (d, $^2J_{PH}$ = 1.2 Hz, 1H, PCH_B), 7.12–7.60 (m, 15H, 3 Ph); 3.25 (s, 3H, MeOH) ppm. $^{13}C\{^1H\}$ NMR ([d_8]THF): δ = 22.76 (s, Me_B), (Me_A superimp. by solvent), 57.81 (d, ^3J = 5.4 Hz, NCH_B), 58.63 (d, ^3J = 9.9 Hz, NCH_A), 60.70 (d, ^1J = 13.6 Hz, PCH_A), 60.94 (d, ^1J = 16.3 Hz, PCH_B), 127.38 (*p*′-CH_B), 127.53 (*p*′-CH_A), 127.68 (2*o*′-CH_B), 128.28 (2*o*′-CH_A), 128.58 (d, ^3J = 6.6 Hz, 4 *m*-CH_A), 128.63, 128.77 (superimposed, 2*m*′-CH_A, 2*m*′-CH_B, 2*m*-CH_B), 128.82 (superimposed d, ^3J = 7.9 Hz, 2*m*-CH_B), 129.03 (*p*-CH_B), 129.14 (*p*-CH_A), 129.69 (*p*-CH_A), 129.81 (*p*-CH_B), 133.95 (d, ^2J = 22.5 Hz, 2*o*-CH_B), 134.08 (d, ^2J = 18.7 Hz, 2*o*-CH_A), 135.19 (d, ^2J = 21.1 Hz, 2*o*-CH_A), 135.31 (d, ^2J = 20.9 Hz, 2*o*-CH_B), 136.46 (d, ^1J = 14.0 Hz, *i*-C_A), 137.10 (d, ^1J = 14.0 Hz, *i*-C_B), ca. 173.20 (d, noise level, COO_B), 173.84 (d, ^2J = 12.6 Hz, COO_A), *i*′-C at noise level; 49.76 (MeOH) ppm. $^{31}P\{^1H\}$ NMR ([d_8]THF): δ = 0.6, −0.03 (A,B, integral ratio 64:36) ppm.

4.5. Diphenylphosphanyl-[(1S)-1-(4-methoxy-phenyl)-ethylamino]-acetic acid methanol solvate (**1d**·MeOH)

A solution of Ph_2PH (1.0 g, 5.37 mmol) and *S*(−)-4-methoxy-α-methylbenzylamine (0.81 g, 5.36 mmol) in diethyl ether (10 mL) was added to a solution of glyoxylic acid hydrate (0.50 g, 5.43 mmol) in diethyl ether. Translucent striations appeared in the solution, then a sticky clump which after stirring for 24 h turned to a precipitate. Filtration, washing with diethyl ether and drying in vacuum gave a white powder, easily soluble in methanol and instantaneously crystallizing as a less soluble methanol solvate. Filtration and drying under vacuum afforded 1.88 g (88%) white powder. Crystallization from MeOH by slow concentration of a saturated solution led to crystals containing only molecules with (1*S*,α*S*)-configuration. Crystal data are compiled in Table 2, selected bond lengths and angles are given in Fig. 1. Anal. Calc. for $C_{23}H_{24}NO_3P{\cdot}CH_3OH$ (425.46): C, 67.75; H, 6.63; N, 3.29; found: C, 67.35; H, 6.35; N, 3.27%. HRMS (ESI in CH_3CN solution): [M+H$^+$] ($C_{24}H_{24}NO_3P$) Calc. 394.1572, found 394.1569. The [d_8]THF solution NMR spectra of **1d**·MeOH displayed two diastereoisomers in a molar ratio 75:25 to 80:20 (by ^{1}H integration). ^{1}H NMR and HH-COSY ([d_8]THF): δ = 1.22 (d, ^3J = 6.5 Hz, 3H, Me_A), 1.23 (d, ^3J = 6.3 Hz, 3H, Me_B), 3.66 (d, ^3J = 6.5 Hz, 1H, NCH_A), 3.70 (s, 3H, OMe_B), 3.71 (superimp. d, ^3J = 6.3 Hz, 1H, NCH_B), 3.74 (s, 3H, OMe_A), 3.77 (d, $^2J_{PH}$ = 3.3 Hz, 1H, PCH_A), 4.17 (d, $^2J_{PH}$ = 1.2 Hz, 1H, PCH_B), 4.2–6.2 (s br, 3H, NH, OH), 6.75 (m, 2H, *m*'-H_A), 6.78 (m, 2H, *m*'-H_B), 7.08 (m, 2H, *o*'-H2 H, 2'-CH_A), 6.78 (m, 2H, *o*'-H_B), 7.17–7.31 (m, 6H, *m*-CH, *p*-CH), 7.32–7.43 (m, 4H, *o*-CH_A), 7.50–7.60 (m, 4H, *o*-CH_B); 3.25 (s, 3H, MeOH) ppm. $^{13}C\{^1H\}$ NMR, DEPT-135, CH-COSY ([d_8]THF): δ = 22.87 (Me_B), 25.04 (Me_A), 55.26 (OMe_{AB}), 57.28 (d, ^3J = 9.0 Hz, NCH_B), 57.99 (d, ^3J = 9.8 Hz, NCH_A), 60.64 (d, ^1J = 14.3 Hz, PCH_A), 61.05 (d, ^1J = 16.6 Hz, PCH_B), 114.20 (2 *m*′-CH_A), 114.28 (2*m*′-CH_B), 128.42 (2*o*′-CH_B), 128.65 (superimp. d, *J* = 6.6 Hz, 4*m*-CH_A, 2*m*-CH_B), 128.71 (d, ^3J = 10.3 Hz, 2*m*-CH_B), 129.08 (*p*-CH_B), 129.17 (*p*-CH_A), 129.29 (2*o*′-CH_A), 129.75 (*p*-CH_A), 129.83 (*p*-CH_B), 134.00 (d, ^2J = 18.1 Hz, 2*o*-CH_B), 134.12 (d, ^2J = 18.7 Hz, 2*o*-CH_A), 135.29 (d, ^2J = 21.2 Hz, 2*o*-CH_A), 135.39 (d, ^2J = 21.2 Hz, 2*o*-CH_B), 136.63 (d, ^1J = 15.0 Hz, *i*-C_{qA}), 136.87 (s, *i*′-C_{qA}), 136.98 (d, ^1J = 17.6 Hz, *i*-C_{qB}), 137.28 (d, ^1J = 17.1 Hz, *i*-C_{qA}), 137.83 (d, ^1J = 17.9 Hz, *i*-C_{qB}), 138.47 (s, *i*′-C_{qB}), 159.83 (s, *p*′-C_{qB}), 160.01 (s, *p*′-C_{qA}), 173.32 (d, ^2J = 10.6 Hz, COO_B), 173.96 (d, ^2J = 12.1 Hz, COO_A); 49.85 (s, CH_3OH) ppm. $^{31}P\{^1H\}$ NMR ([d_8]THF): δ = 0.5, −0.1 (A, B, integral ratio 75:25); at −50 °C δ = −2.0, −2.4 (integral ratio 78:22) ppm. After storage for few days or short heating at 40 °C, stronger at 55 °C, signals of decarboxylation products appeared, δ = −19.2, weakly δ = −27.6 ppm.

Table 2
Crystal data and structure refinement of **1d**·MeOH.

Empirical formula	$C_{24}H_{28}NO_4P$
Formula weight	425.44
T (K)	100(2)
Wavelength (Å)	1.54178
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	5.9546(5)
b (Å)	10.3969(7)
c (Å)	36.903(3)
β (°)	92.133(3)
V (Å^3)	2283.0(3)
Z	4
D_{calc} (Mg/m^3)	1.238
Absorption coefficient (mm^{-1})	1.304
F(000)	904
Crystal size (mm^3)	0.28 × 0.11 × 0.05
θ range for data collection	2.40–69.36°
Independent reflections	8765
Completeness to *θ* = 69.36°	97.2%
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.938 and 0.846
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	8765/8/566
Goodness-of-fit on F^2	1.097
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0429, wR_2 = 0.1300
R indices (all data)	R_1 = 0.0441, wR_2 = 0.1373
Absolute structure parameter	0.01(2)
Largest difference peak and hole (e Å^{-3})	0.35 and −0.32

4.6. Diphenylphosphanyl-[(1R)-(1-phenyl-propylamino)]-acetic acid methanol solvate (**1e**·0.6MeOH)

A solution of Ph_2PH (1.01 g, 5.42 mmol) and *R*(+)-α-ethylbenzylamine (0.77 g, 5.69 mmol) in diethyl ether (10 mL) was added to a solution of glyoxylic acid hydrate (0.50 g, 5.43 mmol) in diethyl ether. After few minutes a white precipitate formed. It was separated after stirring the mixture overnight, washed with diethyl ether and dried in vacuum to give 1.60 g (78%) white powder. Crystallization from MeOH gives small colorless crystals of a solvate with ca. 0.6 MeOH per molecule, mp. (dec.) 97–100 °C. Anal. Calc. for $C_{23}H_{24}NO_2P{\cdot}0.6CH_3OH$ (396.65): C, 71.46; H, 6.71; N, 3.53; found: C, 71.61; H, 6.60; N, 3.41%. The [d_8]THF solution NMR spectra displayed two diastereoisomers in a molar ratio A:B of 75:25 to 80:20 (by ^{1}H integration). ^{1}H NMR ([d_8]THF): δ = 0.66 (t, ^3J = 7.5 Hz, 3H, $CH_{3\ B}$), 0.72 (t, ^3J = 7.5 Hz, 3H, $CH_{3\ A}$), 1.45–1.81 (m, 4H, $CH_{2\ AB}$), 3.44 (t br, ^3J = 6.8 Hz, 1H, NCH_A), 3.49 (superimp. t, 1H, NCH_B), 3.75 (d, $^2J_{PH}$ = 3.3 Hz, 1H, PCH_A), 4.14 (br s, 1H, PCH_B), 7.11–7.43 (m, 14H, Ph), 7.50–7.57 (m, 1H, Ph); 3.25 (s, 2.5H, 0.6 MeOH) ppm. $^{13}C\{^1H\}$ NMR ([d_8]THF): δ = 10.76 (s, $CH_{3\ B}$), 10.82 (s, $CH_{3\ A}$), 30.12 (s, $CH_{2\ B}$), 31.91 (s, $CH_{2\ A}$), 60.35 (d, ^1J = 14.5 Hz, PCH_A), 61.16 (d, ^1J = 17.2 Hz, PCH_B), 64.75 (d, ^3J = 8.9 Hz, NCH_B), 65.29 (d, ^3J = 9.4 Hz, NCH_A), 127.57 (*p*′-CH_B), 127.76 (*p*′-CH_A), 128.24, 128.74 (*o*′-CH_B, *m*′-CH_B), 128.57 (d, ^3J = 6.4 Hz, 2*m*-CH_A), 128.60 (d, ^3J = 9.5 Hz, 2*m*-CH_A), ca. 128.62 (superimp. d, ^3J = 6 Hz, 2*m*-CH_B), 128.69, 128.99 (*o*′-CH_A, *m*′-CH_A), 129.07 (*p*-CH_B), 129.15

(p-CH_A), 129.68 (sh, p-CH_B), 129.70 (p-CH_A), 134.10 (superimp. d, ^2J = 18.8 Hz, 2o-CH_A, 2o-CH_B), 135.18 (d, ^2J = 21.1 Hz, 2o-CH_A), 135.20 (d, ^2J = 20.8 Hz, 2o-CH_B), 136.46 (d, ^1J = 15.1 Hz, i-C_{qA}), 136.92 (d, ^1J = 17.2 Hz, i-C_{qB}), 136.98 (d, ^1J = 17.2 Hz, i-C_{qA}), 137.64 (d, ^1J = 17.6 Hz, i-C_{qB}), 143.69 (i-C'_{qA}), 144.67 (i-C'_{qB}), 173.08 (d, ^2J = 9.7 Hz, $COOH_B$), 175.79 (d, ^2J = 12.3 Hz, $COOH_A$); 49.76 (MeOH) ppm. $^{31}P\{^1H\}$ NMR ([d_8]THF): δ = 0.4, −0.6 (A, B, integral ratio 80:20) ppm.

4.7. Diphenylphosphanyl-[(1R)-(1-naphthalen-1-yl-ethylamino)-acetic acid methanol solvate (**1f**·MeOH)

A solution of glyoxylic acid hydrate (0.54 g, 5.80 mmol) in diethyl ether (20 mL) was added to a solution of Ph_2PH (1.09 g, 5.85 mmol) and R(+)-1-(naphth-1-yl)ethylamine (0.99 g, 5.77 mmol) in diethyl ether (10 mL). A precipitate formed immediately which dissolved after 15 min to give a sticky, pale yellow clump. After 15 h the ether was decanted off and the substance washed with ether. On drying in vacuum a foam was formed. Methanol was added in 10 mL portions (in total 40 mL). The substance dissolved only partially and on shaking formed a suspension of the methanol solvate. This was filtered, washed with diethyl ether and dried in vacuum to give 1.36 g (53%) white powder. Anal. Calc. for $C_{26}H_{24}NO_2P{\cdot}CH_3OH$ (445.49): C, 72.79; H, 6.34; N, 3.14; found: C, 72.45; H, 6.31; N, 3.22%. $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 0.78, 0.44 (A, B, integral ratio 80:20) ppm. Attempts at crystallization from warm methanol led to partial decomposition, with occurrence of signals from Ph_2PD and decarboxylation products.

4.8. Diphenylphosphanyl-[(1S)-(1-naphthalen-**2**-yl-ethylamino)-acetic acid methanol solvate (**1g**·MeOH)

A solution of Ph_2PH (1.0 g, 5.37 mmol) and S(−)-1-(naphth-2-yl)ethylamine (0.85 g, 4.96 mmol) in diethyl ether (10 mL) was added to a solution of glyoxylic acid hydrate (0.50 g, 5.43 mmol) in diethyl ether. Translucent striations appeared in the solution, then a sticky clump, which after stirring for 24 h converted to a precipitate. This was filtered off, washed with diethyl ether and dried in vacuum. The white powder was easily soluble in methanol (40–50 mL) and instantaneously formed a less soluble methanol solvate. Filtration and drying under vacuum afforded 1.92 g (87% ref. to amine) microcrystals. Anal. Calc. for $C_{26}H_{24}NO_2P{\cdot}CH_3OH$ (445.49): C, 72.79; H, 6.34; N, 3.14; found: C, 72.63; H, 5.96; N, 3.07%. The solution NMR spectra in [d_8]THF displayed two diastereoisomers in a molar ratio A:B of ca. 67:33 (by ^1H integration). ^1H NMR ([d_8]THF): δ = 1.39 (d, ^3J = 6.6 Hz, 3H, Me_A), 1.40 (d, ^3J = 6.4 Hz, 3H, Me_B), 3.90 (d, $^2J_{PH}$ = 2.9 Hz, 1H, PCH_A), 4.31 (d, $^2J_{PH}$ = 1.1 Hz, 1H, PCH_B), 4.62 (2 q superimposed, ^3J = 6.4 Hz, 2H, $CHMe_{AB}$), 7.10–8.20 (m, 17H, aryl); 3.25 (s, 3H, MeOH) ppm. $^{13}C\{^1H\}$ NMR ([d_8]THF): δ = 22.0 (s, Me_B), 24.55 (s, Me_A), ca. 54.6 (d br, ^3J = 10 Hz, NCH_{AB}), 60.73 (d, ^1J = 17.3 Hz, PCH_B), 61.12 (d, ^1J = 14.5 Hz, PCH), 123.76, 124.01, 124.04, 125.20, 125.73, 125.84, 126.12, 126.15, 126.27, 127.91, 127.96 (CH, $naph_{AB}$), 128.59 (d, ^3J = 6.7 Hz, m-CH_A), 128.68 (d, ^3J = 6.5 Hz, m-CH_A), 128.73 (d, ^3J = 6.6 Hz, m-CH_B), 129.12, 129.36 129.36, 129.43, 129.68, 129.78 (CH, $naph_{AB}$ and p-CH_{AB}), 132.52 (C_q, $naph_A$), 134.03 (d, ^2J = 18.6 Hz, o-CH_B), 134.45 (d, ^2J = 19.7 Hz, o-CH_A), 135.09 (C_q, naphA), 135.15 (d, ^2J = 20.8 Hz, o-CH_A), 135.26 (d, ^2J = 20.6 Hz, o-CH_B), 136.33 (d, ^1J = 14.6 Hz, i-C_{qB}), 136.83 (d, ^1J = 17.0 Hz, i-C_{qA}), 140.76, 142.26 (C_q, $naph_{A,B}$), 173.34 (d, ^2J = 10.6 Hz, COO_A), 174.11 (d, ^2J = 11.7 Hz, COO_B); some signals superimposed, 49.76 (MeOH) ppm. $^{31}P\{^1H\}$ NMR ([d_8]THF): δ = 0.8, 0.1 (A, B, integral ratio 67:33), trace of decarboxylation product δ = −18.4 ppm.

4.9. Ethylene oligomerization

The equipment and procedure for the screening of **1b**·MeOH and **1d**·MeOH in the Ni-catalyzed ethylene oligomerization (batch-test) was the same as reported earlier for other P,O$^-$ ligands [16]. Quantities of catalyst, ethylene and solvents, reaction conditions, yields and characteristic product data are compiled in Table 1.

4.10. Crystal structure analysis of **1d**·MeOH

X-ray diffraction data for **1d**·MeOH were recorded on a Bruker SMART 6000 CCD diffractometer at 100 K using monochromated Cu Kα-radiation. The sample seemed to be optically uniform. Several crystals were inspected, but all proved to be twins. Finally, a dataset was recorded using a crystal twinned by 180° rotation about c^*. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97) [17] using the "HKLF 5" method (all equivalent reflections are merged during the untwinning process, so that the calculated number of reflections may not be reliable). All non-hydrogen atoms were refined anisotropically. The OH and NH hydrogens were refined freely but with distance restraints. Methyls were refined as idealized rigid groups allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions. The absolute configuration was determined unambiguously, with a Flack parameter of 0.01(2).

Acknowledgements

We thank Dr. Cun Yen Guo, Chinese Academy of Sciene Bejing, for ethylene oligomerization tests in the presence of 1-hexene, B. Witt and Dr. M. K. Kindermann for numerous solution NMR measurements, Dr. W. Hemme, Prof. H. Eckert and Dr. K. Meise-Gresch, Institut für Physikalische Chemie Münster, for solid state MAS NMR spectra of **1d**·MeOH, Prof. M. Beller and Dr. S. Enthaler, Leibniz-Institut für Katalyse e.V. (LIKAT Rostock), for hydrogenation screenings and Dr. H. Frauendorf and G. Sommer-Udvarnoki (Georg-August-Universität Göttingen, Institut für Organische und Biomolekulare Chemie) for ESI-HRMS measurement of **1d**·MeOH.

Appendix A. Supplementary data

CCDC 1456453 contains the supplementary crystallographic data for **1d**·MeOH. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.07.011.

References

[1] (a) Selected recent reviews: I.D. Kostas, Adv. Org. Synth. 6 (2013) 3–58;
(b) S. Lühr, J. Holz, A. Börner, ChemCatChem 3 (2011) 1708–1730;
(c) Privileged Chiral Ligands and Catalysts, Zhou, Qi-Lin (Ed.), Wiley-VCH, Weinheim, 2011.;
(d) G. Erre, S. Enthaler, K. Junge, S. Gladiali, M. Beller, Coord. Chem. Rev. 252 (2008) 471–491;
(e) A. Börner (Ed.), Phosphorus Ligands in Asymmetric Catalysis, Wiley-VCH, Weinheim, 2008;
(f) D.S. Glueck, Chem. Eur. J. 14 (2008) 7108–7117;
(g) X. Zhang, Y. Chi, W. Tang, in Comprehensive Organometallic Chemistry III (Eds.: D.M.P. Mingos, R.H. Crabtree), Elsevier, 2007, Vol. 10, pp. 1–70.
[2] Review: K. Kellner, A. Tzschach, Z. Chem. 24 (1984) 365–375.
[3] (a) K. Kellner, A. Tzschach, Z. Nagy-Magos, L. Markó, *J. Organomet. Chem.* 193 (1980) 307–314;
(b) K. Kellner, W. Hanke, A. Tzschach, Z. Nagy-Magos, L. Markó, *J. Organomet.*

Chem. 268 (1984) 175–183;
(c) J. Zhang, J.J. Vittal, W. Henderson, J.R. Wheaton, I.H. Hall, T.S. Andy Hor, Y.K. Yan, *J. Organomet. Chem.* 650 (2002) 123.
[4] (a) A.A. Karasik, I.O. Georgiev, O.G. Sinyashin, E. Hey-Hawkins, Polyhedron 19 (2000) 1455–1459;
(b) A.A. Karasik, I.O. Georgiev, E.I. Musina, O.G. Sinyashin, J. Heinicke, Polyhedron 20 (2001) 3321–3331.
[5] Recent review: E.I. Musina, A.A. Karasik, O.G. Sinyashin, G.N. Nikonov, Heterocyclic Phosphines with P-C-X Fragments (X = O, N, P) in: E.F.V. Scriven, C.A. Ramsden (eds.), Advances in Heterocyclic Chemistry, Academic Press, 2015, pp. 83–130.
[6] (a) P.W. Lednor, W. Beck, H.G. Fick, H. Zippel, Chem. Ber. 111 (1978) 615–628;
(b) A.M.Z. Slawin, J.D. Woollins, Q.J. Zhang, J. Chem. Soc., Dalton Trans., 2001, pp. 621–632.
[7] (a) Reviews: S.R. Gilbertson, Prog. Inorg. Chem. 50 (2001) 433–471;
(b) A. Agarkov, S.J. Greenfield, D. Xie, R. Pawlick, G. Starkey, S.R. Gilbertson, Biopolym, Pept. Sci. 84 (2006) 48–73;
(c) A. Perdih, M. Sollner Dolenc, Curr. Org. Chem. 15 (2011) 3750–3799.
[8] (a) S.R. Gilbertson, G. Chen, M. McLoughlin, J. Am. Chem. Soc. 116 (1994) 4481–4482;
(b) C. Meyer, H. Grützmacher, H. Pritzkow, Angew. Chem. Int. Ed. 36 (1997) 2471–2473;
(c) M. Tepper, O. Stelzer, T. Häusler, W.S. Sheldrick, Tetrahedron Lett. 38 (1997) 2257–2258;
(d) D.J. Brauer, S. Schenk, S. Roßenbach, M. Tepper, O. Stelzer, T. Häusler, W.S. Sheldrick, J. Organomet. Chem. 598 (2000) 116–126;
(e) D.J. Brauer, K.W. Kottsieper, S. Schenk, O. Stelzer, Z. Anorg. Allg. Chem. 627 (2001) 1151–1156;
(f) C. Meyer, M. Scherer, H. Schönberg, H. Rügger, S. Loss, V. Gramlich, H. Grützmacher, Dalton Trans. (2006) 137–148.
[9] (a) J. Heinicke, N. Peulecke, P.G. Jones, Chem. Commun. (2005) 262–264;
(b) J. Lach, C.-Y. Guo, M.K. Kindermann, P.G. Jones, J. Heinicke, Eur. J. Org. Chem. (2010) 1176–1186;
(c) O.S. Fomina, D.G. Yakhvarov, J. Heinicke, O.G. Sinyashin, *Uchenye zapiski Kazanskogo Universiteta* (*Proceedings of the Kazan University*) 154 (3) (2012) C13–C27;
(d) J. Lach, N. Peulecke, M.K. Kindermann, G.J. Palm, M. Köckerling, J.W. Heinicke, Tetrahedron 71 (2015) 4933–4945.
[10] F. Chastrette, C. Bracoud, M. Chastrette, G. Mattioda, Y. Christidis, Bull. Soc. Chim. Fr. II (1985) 66–74.
[11] (a) N. Peulecke, M.K. Kindermann, M. Köckerling, J. Heinicke, Polyhedron 41 (2012) 61–69;
(b) K.R. Basvani, O.S. Fomina, D.G. Yakhvarov, J. Heinicke, Polyhedron 67 (2014) 306–313.
[12] (a) D.L. Davies, J. Neild, L.J.S. Prouse, D.R. Russell, Polyhedron 12 (1993) 2121–2124;
(b) A.L. Balch, M.M. Olmstead, S.P. Rowley, Inorg. Chim. Acta 168 (1990) 255–264.
[13] J.A. van Doorn, N. Meijboom, J. Chem. Soc. Perkin Trans. 2 (1989) 1309–1313.
[14] (a) M. Peuckert, W. Keim, Organometallics 2 (1983) 594–597;
(b) W. Keim, R.P. Schulz, *J. Mol. Catal.* 92 (1994) 21–33;
(c) J. Heinicke, N. Peulecke, M. Köhler, M. He, W. Keim, J. Organomet. Chem. 690 (10) (2005) 2449–2457;
(d) P. Kuhn, D. Semeril, D. Matt, M.J. Chetcuti, P. Lutz, Dalton Trans. (2007) 515–528;
(e) W. Keim, Angew. Chem. Int. Ed. 52 (2013) 12492–12496.
[15] K. Issleib, A. Tzschach, Chem. Berichte 92 (1959) 1118–1126.
[16] J. Heinicke, M. Köhler, N. Peulecke, M. He, M.K. Kindermann, W. Keim, G. Fink, Chem. Eur. J. 9 (2003) 6093–6107.
[17] G.M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr. 64 (2008) 112–122.