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α-Diphenylphosphino-*N*-(pyrazin-2-yl)glycine as a ligand in Ni-catalyzed ethylene oligomerization

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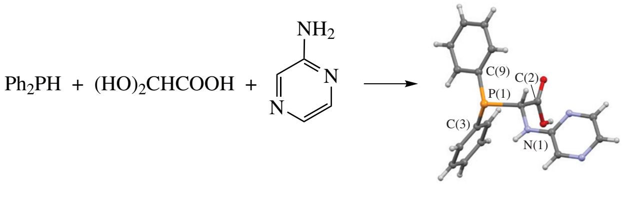
α-Diphenylphosphino-*N*-(pyrazin-2-yl)glycine was synthesized by the three-component condensation of diphenylphosphine, glyoxylic acid hydrate, and 2-aminopyrazine and its structure was confirmed by X-ray diffraction. It reacted with [Ni(COD)$_2$] (COD is cycloocta-1,5-diene) to give complexes that were tested as catalysts for selective dimerization/oligomerization of ethylene to but-1-ene (main product) and C$_6$–C$_{14}$ α-olefins, respectively.

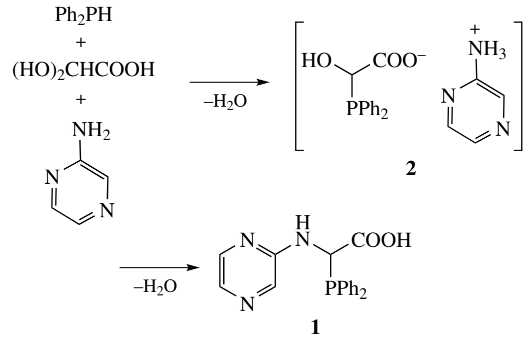


Linear alpha olefins (LAO) are produced in large scale by various industrial processes[1] as base materials for oxo alcohols used in biodegradable detergents and plasticizers (C$_{10}$–C$_{18}$), as comonomers for producing different types of alkyl-branched polyethylenes or lubricants (C$_4$–C$_8$), and as starting materials for other products. The industrial need for short LAOs with four–eight carbon atoms is ever growing and requires new catalysts for oligomerization of ethylene to short LAOs or selective di-,[2] tri- and tetramerization.[3] One of the most important processes for the production of LAOs is the Shell Higher Olefin Process (SHOP) that involves the step of P–C–C–O$^-$–Ni chelate-catalyzed oligomerization of ethylene.[1(*b*),4] Depending on the nature of the P–C–C–O$^-$ ligands, oligomers or polymers are produced;[5] very short linear α-olefins are also obtained in the presence of Ph$_3$P,[6] whereas the exclusive formation of butenes in the absence of this additive is rare for neutral phosphine-based catalysts.[2(*a*)] Highly active acidic P,OR$^+$ or P,OH$^+$–Ni catalysts, producing mainly butenes, are usually less selective and provide mixtures of isomers.[7] Having performed studies on phosphinophenols and their use for generation of Ni catalysts for oligo- or polymerization of ethylene,[5(*a*),8] we focussed on α-phosphino amino acids,[9] in particular, phosphinoglycines[10] readily accessible by three-component one-pot reactions, and their potential to form Ni catalysts for ethylene oligomerization.

Here we describe the synthesis of new *N*-(pyrazin-2-yl)-substituted diphenylphosphinoglycine **1**, its structure and data on ligand screening in the nickel-catalyzed oligomerization of ethylene. Compound **1** was obtained by addition of a solution containing diphenylphosphine and 2-aminopyrazine to a solution of glyoxylic acid hydrate in diethyl ether or methanol or in a mixture of these solvents. The reaction proceeds at room temperature *via* the corresponding pyrazine-ammonium diphenylphosphinoglycolate **2** ($\delta_{^{31}\mathrm{P}}$ = 6.0 ppm), which immediately precipitates in diethyl ether after mixing, and in MeOH it converts slowly to compound **1** (Scheme 1). This formation of **1** *via* **2** corresponds to the usual behaviour of sterically unhindered primary alkylamines or anilines in the three-component reactions.[9,10]

The structure of compound **1** was unambiguously proved by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and by X-ray crystal structure analysis (Figure 1).[†]

Compound **1** crystallizes in the centrosymmetric monoclinic space group *P*2$_1$/*n* with each one molecule with *R*- and *S*-configuration of the α-C atom in the unit cell. The phosphorus atom displays the typical pyramidal configuration, the Newman



Scheme 1 *Reagents and conditions*: Et$_2$O or MeOH, room temperature.

[†] For synthesis and NMR data of **1**, see Online Supplementary Materials. *Crystallographic data for* **1**: crystals of C$_{18}$H$_{16}$N$_3$OP (*M* = 337.31) are monoclinic, space group *P*2$_1$/*n*, at 100 K: *a* = 6.2160(5), *b* = 21.3663(17) and *c* = 12.0547(10) Å, *β* = 102.399(4)°, *V* = 1563.7(2) Å^3, *Z* = 4, d_calc = = 1.433 g cm^{-3}, *μ*(MoK*α*) = 0.192 mm^{-1}, *F*(000) = 704. 28744 reflections were measured and 3749 independent reflections (R_int = 0.111) were used in a further refinement. The refinement converged to *wR*$_2$ = 0.1693 and GOF = 1.11 for all independent reflections [*R*$_1$ = 0.0550 was calculated against *F* for 2360 observed reflections with *I* > 2*σ*(*I*)].

Table 1 Catalytic homogeneous oligomerization of ethylene catalyzed by [Ni(COD)$_2$]/**1** (~1 : 1 molar ratio) system in THF (125–200 ml per mmol of the catalyst).

Entry	T/°C	[Ni]/mol% to C_2H_4 applied	Conversion of C_2H_4 (%)/ TON	Product composition (%)							S(αC=)^a (%)
				C_4	C_6	C_8	C_{10}	C_{12}	$\Sigma C_{14}–C_{30}$	polymer	
1	25	0.052	10/192	1	1	n.d.^{b}	1	3	9	85	–
2	25	0.035	5/158	1	1^c					98	–
3	80	0.040	69/1763	44	19	13	8	5	5	6	96.2
4	100	0.040^d	41/1464	37	14	7	8	7	24	3	96.4
5	100	0.032	58/2493	24	14	9	10	9	30	3	97.3
6	120	0.045	49/1202	46	26	14	7	3	2	2	99.7

^{a} S(αC=) is selectivity to α-olefins *vs*. internal ones determined by GC-MS as the average for C_{10}–C_{14}. ^{b} Not detected. ^{c} Total for C_6–C_{30} olefins. ^{d} [Ni(COD)$_2$]/**1** ratio was 1.4 : 1.

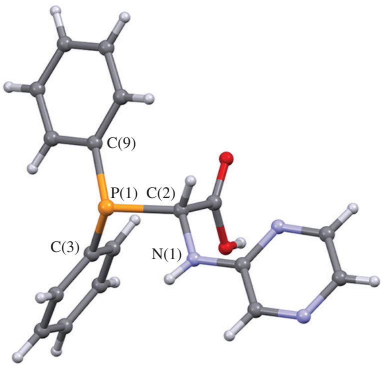


Figure 1 The structure of α-diphenylphosphino-*N*-(pyrazin-2-yl)glycine **1** in the crystal.

projection along the C(2)–P(1) bond shows that one *P*-phenyl group locates in *trans*-position to the C(2)–N(1) bond, the other in *gauche*-position [torsion angles C(9)P(1)C(2)N(1) 177.11°, C(3)P(1)C(2)N(1) –76.91°].

The interesting point with respect to potential use of diphenylphosphinoglycine **1** as a ligand for nickel-catalyzed ethylene oligomerization is that the latter possesses the same P–C–C–O$^-$ structure motive as diphenylphosphinoacetic acid used to obtain high active nickel catalysts for the industrial process of ethylene oligomerization.[1,4] It should be also noted that some phosphinoglycines with various *N*-aryl or *N*-alkyl substituents in combination with [Ni(COD)$_2$] have already been tested in ethylene oligomerization process. However, in case of N-heterocyclic substituents, these attempts have failed due to possible blocking of the catalytically active Ni-center by additional N-coordination of the N-heterocyclic group. A related behaviour is also characteristic of some new water-soluble ligands based on *P*-pyridyl-containing phospholane oxides that are capable to form bis-N,O-chelate nickel(II) complexes.[11]

The investigation of the activity of the catalysts generated from ligand **1** and [Ni(COD)$_2$] in the ethylene oligomerization process was performed in THF as the most suitable solvent.[9,10] At 80–120 °C, short linear α-olefins C_4–C_{14}, containing but-1-ene as the major product, were formed.‡ Figure 2 depicts the experimentally observed kinetic curve of the ethylene consumption, superimposed by the growing vapor pressure of low-boiling ethylene dimers and trimers, at different temperatures. A slight increase in the pressure at 25 °C and formation of small amounts of polymers and traces of oligomers (Table 1, entries 1 and 2) indicate slow exothermic conversion of ethylene already at room temperature. More rapid reaction, as shown by the curve recorded at 80 °C, and higher conversion (entry 3) require moderate heating. Polymers are formed only in traces, while the predominant product is but-1-ene, accompanied by small amounts of linear α-olefins from hex-1-ene to dodec-1-ene. The processing at 100 °C, usual for *N*-aryl- or *N*-alkylphosphinoglycinate Ni catalysts,[10] or even at 120 °C, would slightly diminish the catalyst activity, life cycles and ethylene conversion (entries 4–6).

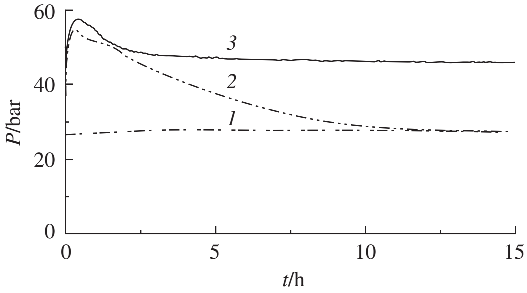


Figure 2 Pressure–time plots for batch oligomerization of ethylene with **1**/[Ni(COD)$_2$] in THF at different bath temperatures: (*1*) 25 °C, (*2*) 80 °C and (*3*) 100 °C.

In summary, catalytic system [Ni]–ligand **1** provides high selectivity towards short linear α-olefins in ethylene oligomerization. This is one of the rare examples of neutral Ni catalysts for generation of mainly but-1-ene among smaller amounts of other linear α-olefins. The known cationic Ni catalysts are usually less selective and produce mixtures of various isomers including branched derivatives.[7] The isolation and characterization of main intermediates of the process and elucidating of the nature of catalytically active species formed in the catalytic process are currently under investigation.

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The measurements were performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo–Kα radiation (λ = = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms.

CCDC 1939537 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

‡ For the details of the catalytic experiments, see Online Supplementary Materials.

This article is dedicated to the memory of Professor Dr. Dr. h.c. Wilhelm Keim.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.033.

References

1 (*a*) G. P. Belov and P. E. Matkovsky, *Pet. Chem.*, 2010, **50**, 283 (*Neftekhimiya*, 2010, **50**, 296); (*b*) W. Keim, *Angew. Chem., Int. Ed.*, 2013, **52**, 12492; (*c*) P.-A. R. Breuil, L. Magna and H. Olivier-Bourbigou, *Catal. Lett.*, 2015, **145**, 173.

2 (*a*) F. Speiser, P. Braunstein and L. Saussine, *Acc. Chem. Res.*, 2005, **38**, 784; (*b*) J. Yu, X. Hu, Y. Zeng, L. Zhang, C. Ni, X. Hao and W.-H. Sun, *New J. Chem.*, 2011, **35**, 178; (*c*) P. Hao, S. Song, T. Xiao, Y. Li, C. Redshaw and W.-H. Sun, *Polyhedron,* 2013, **52**, 1138 and references therein; (*d*) H. Olivier-Bourbigou and L. Magna, in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook*, eds. B. Cornils, W. A. Herrmann, M. Beller and R. Paciello, Wiley, 2017, vol. 1, ch. 5.2, pp. 328–342.

3 (*a*) D. S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J. T. Dixon, A. Bollmann, H. Maumela, F. Hess and U. Englert, *J. Am. Chem. Soc.*, 2003, **125**, 5272; (*b*) D. S. McGuinness, *Chem. Rev.*, 2011, 2321; (*c*) U. Rosenthal, B. H. Müller, N. Peulecke, S. Peitz, A. Wöhl and W. Müller, in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook*, eds. B. Cornils, W. A. Herrmann, M. Beller and R. Paciello, Wiley, 2017, vol. 1, ch. 5.1, pp. 307–327; (*d*) I. E. Nifant'ev, A. A. Vinogradov, A. A. Vinogradov, S. I. Bezzubov and P. V. Ivchenko, *Mendeleev Commun.*, 2017, **27**, 35.

4 (*a*) W. Keim, *Vysokomol. Soedin., Ser. A*, 1994, **36**, 1644 (in Russian); (*b*) M. Peuckert and W. Keim, *Organometallics*, 1983, **2**, 594; (*c*) M. Peuckert, W. Keim, S. Storp and R. S. Weber, *J. Mol. Catal.*, 1983, **20**, 115; (*d*) W. Keim and R. P. Schulz, *J. Mol. Catal.*, 1994, **92**, 21.

5 (*a*) J. Heinicke, N. Peulecke, M. Köhler, M. He and W. Keim, *J. Organomet. Chem.*, 2005, **690**, 2449; (*b*) P. Kuhn, D. Sémeril, D. Matt, M. J. Chetcuti and P. Lutz, *Dalton Trans.*, 2007, 515.

6 (*a*) W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 466; (*b*) W. Keim, A. Behr, B. Gruber, B. Hoffmann, F. H. Kowaldt, U. Kürschner, B. Limbäcker and F. P. Sistig, *Organometallics*, 1986, **5**, 2356; (*c*) J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.*, 1998, 467; (*d*) J. Heinicke, M. Köhler, N. Peulecke and W. Keim, *J. Catal.*, 2004, **225**, 16.

7 (*a*) A. Ecke, W. Keim, M. C. Bonnet, I. Tkatchenko and F. Dahan, *Organometallics*, 1995, **14**, 5302; (*b*) Z. J. A. Komon, X. Bu and G. C. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 12379; (*c*) J. Andrieu, P. Braunstein, F. Naud and R. D. Adams, *J. Organomet. Chem.*, 2000, **601**, 43; (*d*) J. Heinicke, M. Köhler, N. Peulecke, M. K. Kindermann, W. Keim and M. Köckerling, *Organometallics*, 2005, **24**, 344.

8 (*a*) D. G. Yakhvarov, K. R. Basvani, M. K. Kindermann, A. B. Dobrynin, I. A. Litvinov, O. G. Sinyashin, P. G. Jones and J. Heinicke, *Eur. J. Inorg. Chem.,* 2009, 1234; (*b*) C.-Y. Guo, N. Peulecke, K. R. Basvani, M. K. Kindermann and J. Heinicke, *Macromolecules*, 2010, **43**, 1416.

9 (*a*) J. Heinicke, J. Lach, K. R. Basvani, N. Peulecke, P. G. Jones and M. Köckerling, *Phosphorus Sulfur Silicon Relat. Elem.*, 2011, **186**, 666; (*b*) M. Ghalib, J. Lach, O. S. Fomina, D. G. Yakhvarov, P. G. Jones and J. Heinicke, *Polyhedron,* 2014, **77**, 10; (*c*) N. Peulecke, D. G. Yakhvarov and J. W. Heinicke, *Eur. J. Inorg. Chem.*, 2019, 1507.

10 (*a*) J. Lach, C.-Y. Guo, M. K. Kindermann, P. G. Jones and J. Heinicke, *Eur. J. Org. Chem.,* 2010, 1176; (*b*) O. S. Fomina, D. G. Yakhvarov, J. Heinicke and O. G. Sinyashin, *Proceedings of the Kazan University (Uchenye Zapiski Kazanskogo Universiteta)*, 2012, **154**, 13 (in Russian); (*c*) J. Lach, N. Peulecke, M. K. Kindermann, G. J. Palm, M. Köckerling and J. W. Heinicke, *Tetrahedron*, 2015, **71**, 4933; (*d*) O. S. Fomina, J. W. Heinicke, O. G. Sinyashin and D. G. Yakhvarov, *Phosphorus Sulfur Silicon Relat. Elem.*, 2016, **191**, 1478.

11 A. V. Shamsieva, K. R. Trigulova, R. R. Fayzullin, V. V. Khrizanforova, Yu. H. Budnikova, E. I. Musina and A. A. Karasik, *Russ. Chem. Bull., Int. Ed.,* 2018, **67**, 1206 (*Izv. Akad. Nauk, Ser. Khim.*, 2018, 1206).

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