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

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All manipulations with air-sensitive compounds were conducted under nitrogen using Schlenk techniques. Solvents were dried by standard methods and were freshly distilled before use. NMR tubes of samples repeatedly measured over several days were closed by ground glass joints or sealed to avoid slow oxidation by air diffusing through the usual plastic caps. Commercial diphenylphosphine, aminopyrazine, glyoxylic acid monohydrate and bis(cycloocta-1,5-diene)nickel(0) (Sigma-Aldrich) were used as purchased. Glyoxylic acid monohydrate was dissolved in diethyl ether using an ultrasonic bath. NMR spectra were recorded with a multinuclear Bruker ARX300 FT-NMR spectrometer at 300.1 (^{1}H), 75.5 (^{13}C) and 121.5 (^{31}P) MHz in CD_3OD. Chemical shifts (δ) are given in ppm and referenced to tetramethylsilane for ^{1}H and ^{13}C NMR and to H_3PO_4 (85%) for ^{31}P NMR. Elemental analyses were determined with a CHNS-932 analyzer from LECO (standard conditions).

Composition of the oligomerization products was determined by GC-MS analysis using Agilent 7890B GC system equipped with HP-5MS Ultra Inert capillary column (30 m length, 0.25 mm diameter, 0.50 μm film, 5% phenylmethylpolysiloxane) and mass-selective electron ionization detector Agilent 5977B. The following temperature program was used: 35°C for 10 min, 10 ° × min^{-1} to 120 °C, 3 min at 120 °C, 20 ° × min^{-1} to 280 °C, 10 min at 280 °C. The corresponding retention times are the following: 2.0 min (but-1-ene), 2.9 min (hex-1-ene), 8.8 min (oct-1-ene), 16.7 min (dec-1-ene), 21.0 min (dodec-1-ene), 24.5 min (tetradec-1-ene), 26.4 min (hexadec-1-ene), 27.7 min (octadec-1-ene). To determine the content of but-1-ene, C_4-fraction was additionally collected by evaporation of butenes at room temperature, collected in cooling trap (-40 °C) and analyzed by gas chromatography using Chromos GCh-1000 equipped with ValcoPLOT VP-Alumina/KCl capillary column (50 m length, 0.53 mm diameter, 10 μm film) and flame ionization detector. The following temperature program was used: 80 °C for 10 min. The corresponding retention times are the following: 6.97 min (2-methylprop-1-ene), 7.16 min (but-1-ene), 8.13 min (*cis*-but-2-ene), 8.90 min (*trans*-but-2-ene).

Turnover number (TON) was calculated as the ratio of the amount of ethylene reacted to the amount of nickel used for catalytic test according to the formula:

$$TON = \frac{m_{oligomers}}{28 \cdot n_{Ni}}$$

X-ray diffraction analysis was performed on automatic diffractometer "Bruker Smart APEX II CCD (λMoK_{α}). The structure was solved by direct method using SIR program[S1] and refined by the full matrix least-squares using SHELXL-97 program.[S2] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed into the geometrically calculated positions and refined as riding atoms. Hydrogens of P-atoms, located in Fourier maps, were refined isotropically. All calculations were performed using WinGX.[S3] Intermolecular interactions were analyzed using the program PLATON.[S4] All the figures were produced by the MERCURY program.[S5]

*a) Preparation of α-diphenylphosphino-N-(pyrazin-2-yl)glycine (**1**) in diethyl ether.* Glyoxylic acid hydrate (1.08 g, 11.7 mmol) was dissolved in diethyl ether (50 ml) and added to a mixture of diphenylphosphine (1.97 ml, 11.3 mmol) and aminopyrazine (1.08 g, 11.4 mmol) in diethyl ether (20 ml). Precipitation of a sticky solid started immediately. After stirring of the mixture for 3 days the solid filtered off, washed with Et_2O and dried under vacuum to give a yellow powder. This was recrystallized from methanol yielding 2.49 g (65%) of compound **1**.

^{1}H NMR (CD_3OD): δ = 3.66 (br, PCH, weak by H/D exchange, PCH), 5.63 (br s, 1 H, NH), 7.27-7.38 (m, 6 H, *o*-H, *p*-H of Ph), 7.50-7.65, (m, 4 H, *m*-H of Ph), 7.64 (d, $J \approx 3$ Hz, 1 H, pyraz), 7.92 (m, 2 H, pyraz) ppm (Figure S1).

$^{13}C\{^1H\}$ NMR (CD_3OD): δ = 54.56 (d, $^1J_{PC}$ = 22.5 Hz, PCH; P^{13}CD multiplet at noise level), 129.34 (d, $^3J_{PC}$ = 5.3 Hz, 2 *m*-CH_A), 129.49 (d, $^3J_{PC}$ = 6.6 Hz, 2 *m*-CH_B), 130.32 (br, *p*-CH), 132.68, 134.44 (2 s, CH-3, CH-5), 134.70 (d, $^2J_{PC}$ = 19.9 Hz, 2 *o*-CH_A), 135.23 (d, $^2J_{PC}$ = 19.9 Hz, 2 *o*-CH_B), 136.19 (d, $^1J_{PC}$ = 15.9 Hz, *i*-C_{qA}), 136.13 (superimposed d, $^1J_{PC} \approx 16.0$ Hz, *i*-C_{qB}), 142.90 (s, CH-6), 155.73 (d, $^3J_{PC}$ = 4.0 Hz, C_q-2), 174.16 (d, $^2J_{PC}$ = 10.6 Hz, COOH) ppm (Figure S2).

$^{31}P\{^{1}H\}$ NMR (CD_3OD): δ = 1.9, 2.2 ppm (integrals 38/62) (Figure S3).

Mass spectrum (ESI^{-}): m/e = 338.1 (10), 337.0 (20), 336.0 (15), 186.0 (95), 185.0 (100); $C_{18}H_{16}N_3O_2P$ $[M]^{+}$ calc. 337.098.

IR (KBr): ν = 3434 (wm), 3002 (wm), 2936 (wm), 2360 (w), 2341 (w), 1699 (st), 1605 (vst), 1496 (wm), 1464 (st), 1435 (st), 1372 (st), 1292 (m), 1249 (vst), 1178 (m), 1027 (st) cm^{-1}.

Calc. for $C_{18}H_{16}N_3O_2P$ (M = 337.32 g × mol^{-1}): C, 64.09, H, 4.78, N, 12.46; found: C, 63.96, H, 4.67, N, 12.37.

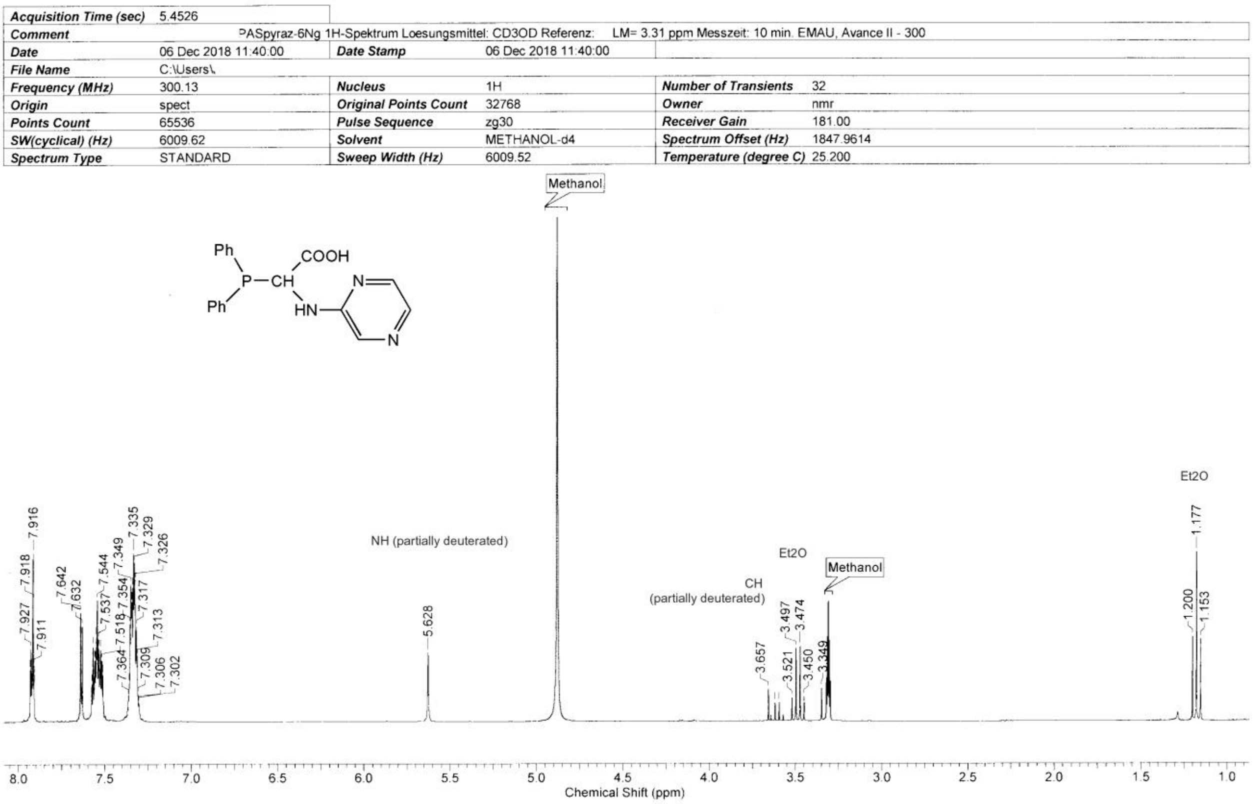

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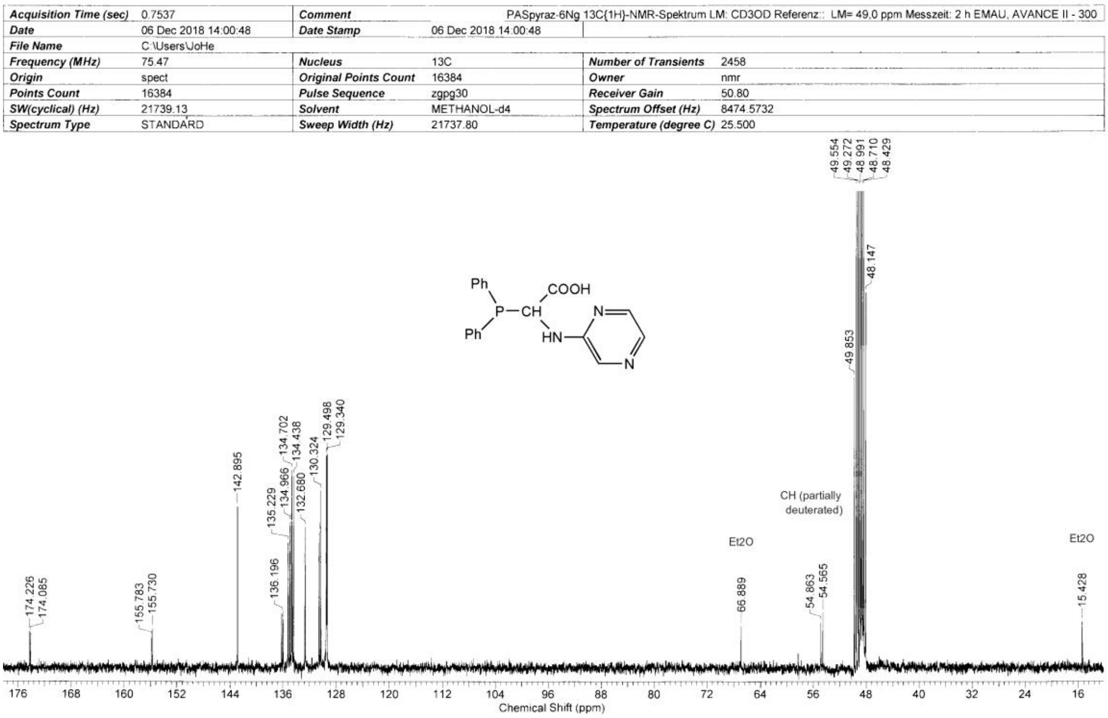
Figure S1. ^{1}H NMR spectrum of α-diphenylphosphino-*N*-(pyrazin-2-yl)glycine



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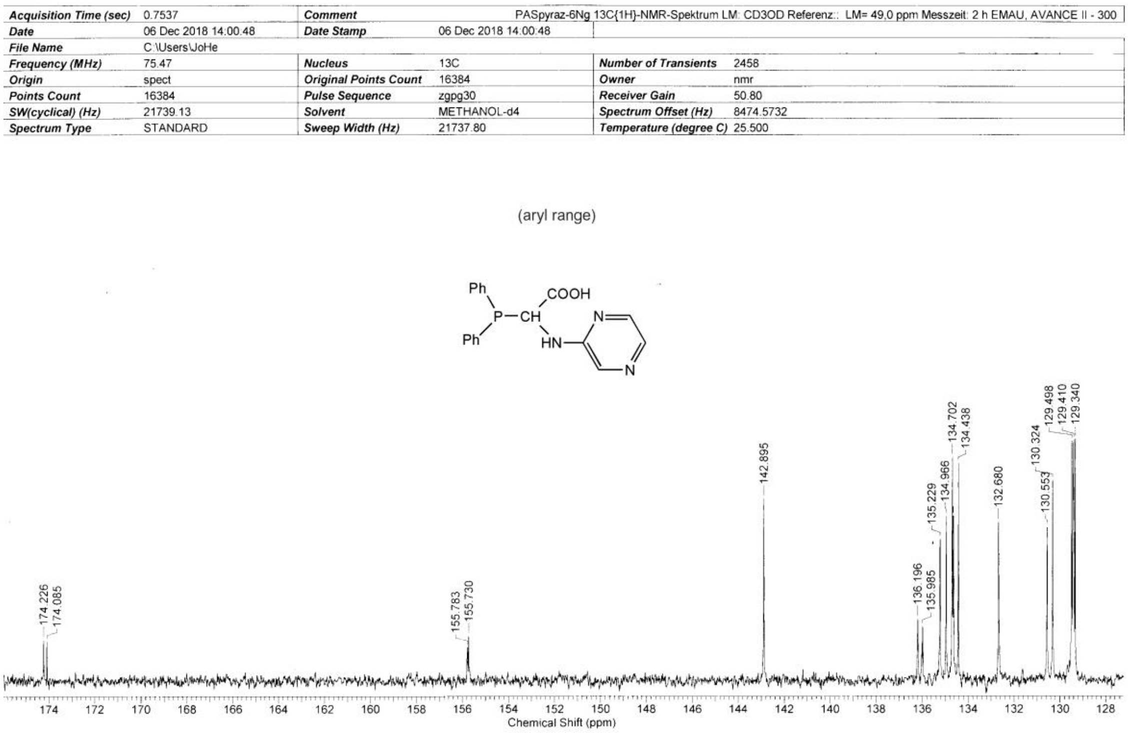
a



Acquisition Time (sec)	0.7537	**Comment**	PASpyraz-6Ng 13C{1H}-NMR-Spektrum LM: CD3OD Referenz:: LM= 49,0 ppm Messzeit: 2 h EMAU, AVANCE II - 300		
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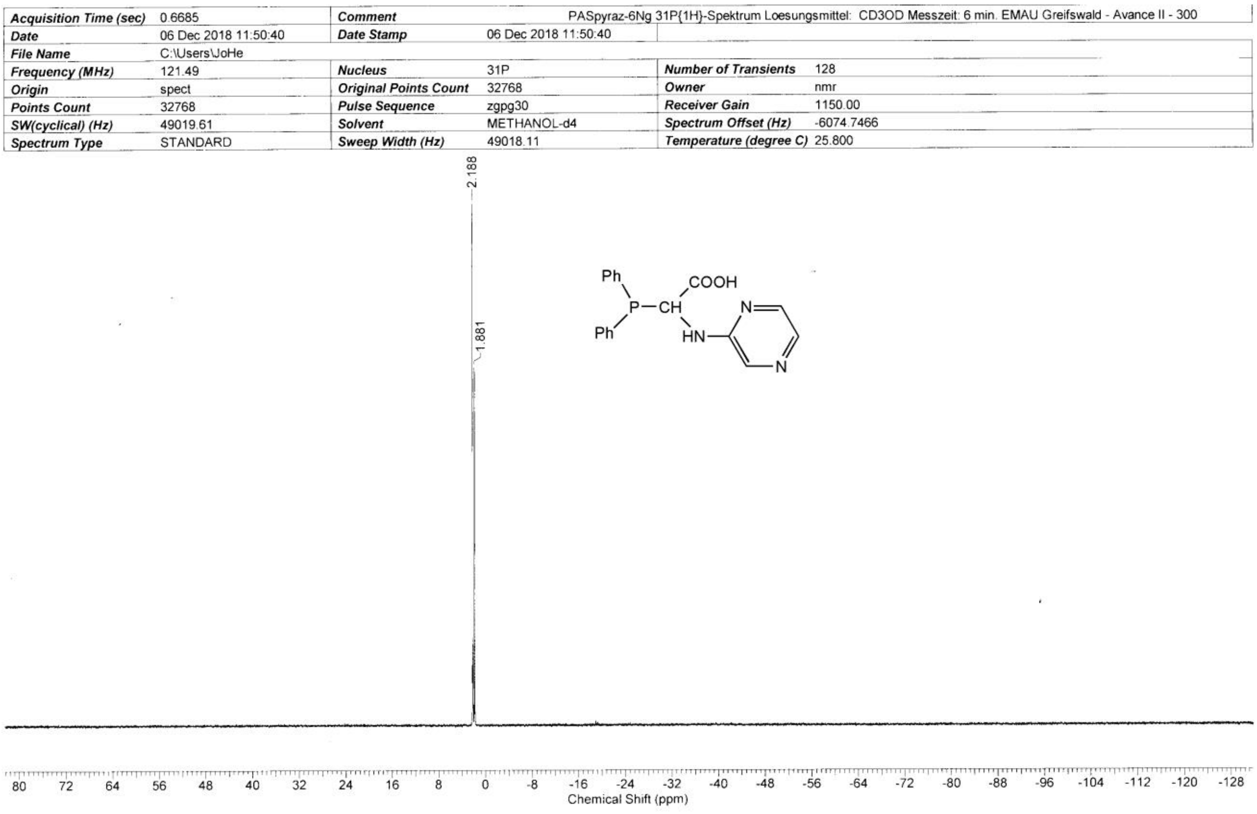
Origin	spect	**Original Points Count**	16384	**Owner**	nmr
Points Count	16384	**Pulse Sequence**	zgpg30	**Receiver Gain**	50.80
SW(cyclical) (Hz)	21739.13	**Solvent**	METHANOL-d4	**Spectrum Offset (Hz)**	8474.5732
Spectrum Type	STANDARD	**Sweep Width (Hz)**	21737.80	**Temperature (degree C)**	25.500

b

Figure S2. ^{13}C NMR spectrum of α-diphenylphosphino-*N*-(pyrazin-2-yl)glycine, full range (a) and selected aryl range (b)



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Spectrum Type	STANDARD	**Sweep Width (Hz)**	49018.11	**Temperature (degree C)**	25.800

Figure S3. ^{31}P NMR spectrum of α-diphenylphosphino-*N*-(pyrazin-2-yl)glycine

*b) Preparation of α-diphenylphosphino-N-(pyrazin-2-yl)glycine (**1**) in the mixture methanol/diethyl ether.* Glyoxylic acid hydrate (264 mg, 2.87 mmol) was dissolved in MeOH (2.0 ml) and this solution was diluted with diethyl ether (20 ml) and added to a solution of aminopyrazine (273 mg, 2.87 mmol) and diphenylphosphine (0.5 ml, 2.87 mmol) in methanol (2.0 ml). Precipitation was not observed. After keeping at room temperature (~22 °C) for 16 h, the solvent was removed under vacuum to leave pale-yellow solution and a viscous yellow-brown substance. Dissolving of the obtained substance in 0.5 ml MeOH and addition of Et_2O caused precipitation of a viscous oil, which after stirring for 10 days formed a suspension. Filtration, washing the solid with Et_2O and drying under vacuum gave 0.44 g (45%) of compound **1**.

c) Reaction in methanol. Glyoxylic acid hydrate (1.0 g, 10.5 mmol) was dissolved in methanol (10 ml) and added to a mixture containing diphenylphosphine (1.83 ml, 10.5 mmol) and aminopyrazine (1.0 ml, 10.5 mmol) in methanol (15 ml). The mixture was stirred at room temperature for 1 day, and the formed precipitate was filtered off. After washing of the precipitate with diethyl ether and drying under vacuum, pale yellow powder of **1** (3.40 g, 95%) was obtained. Dissolving of a small amount of the obtained product in methanol and leaving this saturated solution for one week led to formation of monocrystals of **1** suitable for X-ray crystal structure analysis.

*Crystal structure analysis of α-diphenylphosphino-N-(pyrazin-2-yl)glycine (**1**).* $C_{18}H_{16}N_3OP$ (M = 337.31) monoclinic, space group $P2_1/n$, 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 = 0.192 mm^{-1}, R_{int} = 0.111, θ_{max} 28.0, Bruker Smart Apex II CCD diffractometer, 28744 reflections collected, 2360 observed reflections with $I > 2\sigma(I)$, final R 0.0550, wR_2 0.1693, 3749 independent reflections with $F^2 \geq 2\sigma(I)$, S = 1.11. The selected bond lengths and angles for **1** are mentioned in Table S1.

Table S1. Selected bond lengths (Å) and angles (°) for compound **1**.

Bond lengths, Å		Angles, °	
P(1)-C(2)	1.880(3)	P(1)-C(2)-N(1)	107.54(18)
P(1)-C(3)	1.829(3)	P(1)-C(2)-C(1)	116.61(17)
P(1)-C(9)	1.830(3)	C(3)-P(1)-C(2)	104.83(14)
N(1)-C(2)	1.453(4)	C(3)-P(1)-C(9)	101.41(15)
N(1)-C(15)	1.353(4)	C(2)-P(1)-C(9)	103.82(14)
C(1)-C(2)	1.520(4)	N(1)-C(2)-C(1)	112.7(2)
C(1)-O(1)	1.215(4)	C(2)-C(1)-O(1)	122.4(3)
C(1)-O(2)	1.329(4)	C(2)-C(1)-O(2)	113.8(3)

Ethylene oligomerization.

33.7 mg (0.1 mmol) of compound **1** (sample obtained in MeOH) and 27.5 mg (0.1 mmol) of the complex [Ni(COD)$_2$], where COD – cycloocta-1,5-diene, were dissolved in THF (each in 10 mL) in separated Schlenk flasks and then mixed by adding of mixture containing **1** to solution of [Ni(COD)$_2$]. The resulting yellow-brown solution was stirred at room temperature for 5 min and transferred through a Teflon® tube to the pre-weighed and argon filled steel autoclave (working volume 75 ml) supplied with magnetic stirrer. The autoclave was equipped with electronic pressure sensor connected to the computer. After weighing, the autoclave was pressurized with ethylene (30–50 bar), weighed again (to determine the amount of ethylene added) and was placed to the silicon bath thermostated at temperatures 25, 80, 100 or 120 °C for 15 h. After this time the autoclave was cooled to -40 °C and unconverted ethylene was removed. Then autoclave was again weighed to determine the weight of the oligomers formed and, based on this, the amount of ethylene converted. The butene fraction was collected in cooling trap (-40 °C) by removing of the butene fractions from the autoclave at room temperature and analyzed by GC analysis. The other volatile products were flash-distilled at 80°C/4.0 mbar from the reaction mixture to the cooling trap (-196°C, liquid nitrogen) and were analyzed by GC-MS. The residual rest of waxy oligomers and some polymers was treated for 1 day with methanol/hydrochloric acid (1:1), then thoroughly washed with methanol, dried in vacuum and was weighed.

References

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