

Palladium Complexes with Bidentate P,N Ligands: Synthesis, Characterization and Application in Ethene Oligomerization

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Palladium complexes of two different P,N ligands (a phosphane–pyridine and a phosphane–imine ligand) were synthesized and characterized. Single crystal X-ray structure analyses of the palladium diiodide compounds revealed a square-planar coordination geometry at the metal center with a longer Pd–I bond in *trans*-position to the phosphorus atom. The chloro-methyl palladium species of the phosphane–pyridine ligand was applied for the oligomerization of ethene using a borate salt as cocatalyst.

Introduction

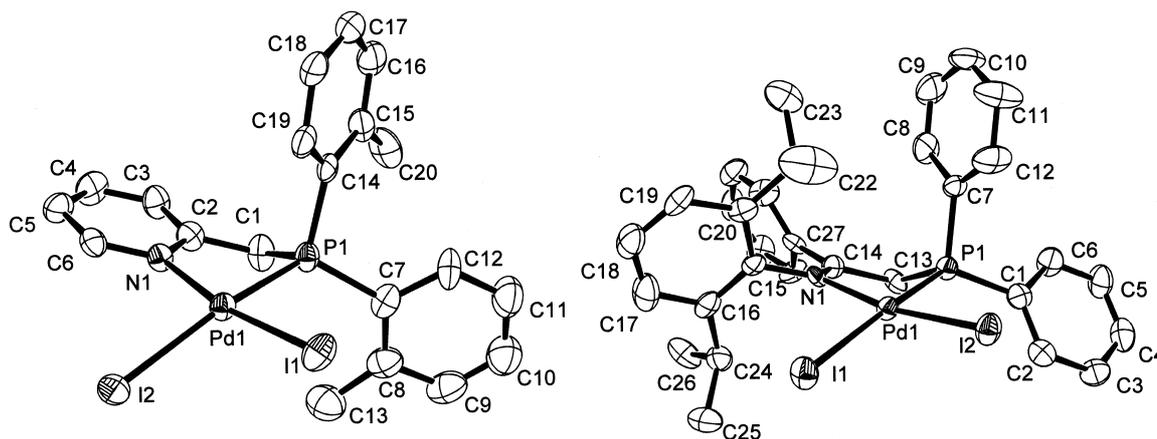
Complexes of the nickel group are well known catalysts for late transition metal catalyzed polymerization reactions [1–7]. Bidentate chelating ligands are often used to fix the active coordination sites of Pd(II) and Ni(II) complexes in a *cis*-arrangement. P,O ligands which are used in the industrial SHOP Process, P,P and N,N ligands are applied in catalytic olefin homo- and copolymerization reactions [2–8, 11 and references cited therein]. P,P palladium complexes are among the most active and most stable catalysts for olefin/CO copolymerizations [5–7]. Ligands with nitrogen functionalities are used in olefin/CO copolymerizations as well as in olefin homopolymerizations [1, 5, 8–11]. In a series of publications the influence of bulky imine substituents on the polymerization properties (activity of the catalyst as well as molecular weight of the isolated polymer) was described [1, 8, 12]. Molecular modeling results suggest that bulky substituents retard the rate of chain transfer reactions [1, 8, 13, 14] and recent investigations have shown that this concept can also be applied to palladium complexes with bis(arylphosphane) ligands. Such complexes catalyze the oligomerization/polymerization of ethene, and the molecular weight of the products is in direct relation with the substitution pattern of the

ligands [15–18]. With respect to our recent investigations with different N,N and P,P ligands, we prepared the bidentate P,N ligands **1** and **2**, consisting of a pyridine and a bis(2-methyl-phenyl) substituted phosphane, or an imine and a diphenylphosphane unit, respectively [19]. To investigate their catalytic properties several palladium complexes of ligands **1** and **2** were synthesized (Fig. 1).

Results and Discussion

Synthesis and characterization

The P,N ligands **1** and **2** as well as the corresponding palladium complexes were synthesized as depicted in Fig. 1. Treatment of 2-(chloromethyl)pyridine with one equivalent of bis(2-methyl-phenyl)phosphane in the presence of potassium *tert*-butanolate yielded ligand **1** which was directly converted to the palladium diiodide complex **3**. Purification of **3** was achieved by column chromatography. The free ligand **1** was regenerated by treating **3** with an excess of potassium cyanide. Reaction of **1** with (COD)PdClMe afforded the chloro-methyl palladium complex **4**. In square-planar (P,N)PdClMe complexes two isomers can be formed (Me *cis* or *trans* to P). In the case of **4** the formation of a single species was observed [20]. In square-planar palladium complexes li-

Fig. 2. Molecular structure of **3** (left) and **6** (right).Table 1. Selected bond lengths and angles of complex **3** and **6**.

3	Bond lengths [Å]		Bond angles [Å]	
	I1–Pd1	2.573(1)	N1–Pd1–P1	83.2(2)
I2–Pd1	2.6608(8)	P1–Pd1–I1	90.22(5)	
Pd1–N1	2.100(5)	N1–Pd1–I2	94.6(1)	
Pd1–P1	2.230(2)	I1–Pd1–I2	93.11(3)	
6	Bond lengths [Å]		Bond angles [Å]	
	I1–Pd1	2.653(1)	N1–Pd1–P1	81.9(3)
I2–Pd1	2.574(1)	P1–Pd1–I2	92.18(8)	
Pd1–N1	2.131(9)	N1–Pd1–I1	94.7(2)	
Pd1–P1	2.223(3)	I2–Pd1–I1	92.14(4)	

The Pd–I bonds *trans* to the phosphorus atoms (Pd1–I2 in **3** and Pd1–I1 in **6**) are longer (0.08 and 0.09 Å) than the Pd–I bonds *trans* to the nitrogen atoms which might be attributed to the larger *trans* influence of the phosphorus atoms as compared to nitrogen atoms (imine and pyridine) [21].

In the solid state one of the *ortho*-aryl substituents (methyl in the case of **3** and isopropyl in the case of **6**) is oriented above/below the coordination planes, occupying the space along the *z*-axis. A connection between shielding of the metal center and chain transfer reactions was found for several N,N complexes [1, 8, 12, 13, 14].

Polymerization reactions

Different P,N ligands were applied in olefin polymerization as well as in olefin/CO copolymerization reactions [2, 19, 24–27]. Complex **4** was tested for ethene polymerization in CH₂Cl₂ after activation of the complex with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAF) in diethyl ether. Runs were performed at 10 and 60 bar. The reaction products were characterized by GC-MS which was calibrated using commercially available 1-olefins (1-octene, 1-decene and 1-dodecene) as standards. Oligomers with molecular weights between 112 g/mol (C₈) and 448 g/mol (C₃₂) were detected. Signals of lower molecular weight compounds were overlapped by the solvent-signal. Olefins with a chain length C_n > 32 were only present in minor quantities (< 1%). As expected, only signals for olefins with an even number of carbon atoms were observed. In the GC-MS spectra for each C_n-fraction (C₈–C₃₂) one intense as well as several less intense signals were detected. We attribute the main signal to the linear 1-olefin (in accordance with our linear standards used for calibration). An influence of the polymerization pressure on the isomer distribution was not observed. At 10 and 60 bar the content of 1-octene within the C₈-fraction was between 94 and 98% [28].

The catalyst system **4**/NaBAF, as well as the corresponding palladium systems containing the P,P ligand 1,3-bis[bis(2-methyl-phenyl)phosphino]pro-

Table 2. Crystallographic data for **3** and **6**.

	3	6
Molecular formula	C ₂₀ H ₂₀ I ₂ NPPd	C ₃₂ H ₃₄ I ₂ NPPd
Formula weight [g/mol]	665.54	823.77
Crystal color and form	red prism	red plate
Crystal system	monoclinic	orthorhombic
Space group	<i>P2₁/n</i>	<i>Pna2₁</i>
<i>a</i> [Å]	9.657(4)	21.936(4)
<i>b</i> [Å]	16.288(3)	13.793(5)
<i>c</i> [Å]	14.258(4)	10.128(5)
β [°]	108.50(3)	90
Volume [Å ³]	2126.8(11)	3064(2)
<i>Z</i>	4	4
<i>D</i> _{calcd.} [mg/m ³]	2.079	1.786
Absorption coefficient [mm ⁻¹]	3.854	2.694
<i>F</i> (000)	1256	1600
Crystal size [mm]	0.24 × 0.22 × 0.15	0.40 × 0.24 × 0.08
θ _{max} [°]	25.24	
2 θ _{max}	25.25	
Number of collected reflections	4054	4041
Number of observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	3220	3496
Number of unique reflections	3815	3825
Number of parameters	226	334
Index range	0 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 19 -17 ≤ <i>l</i> ≤ 16	-21 ≤ <i>h</i> ≤ 26 -13 ≤ <i>k</i> ≤ 16 -12 ≤ <i>l</i> ≤ 5
Goodness-of-fit on <i>F</i> ²	1.065	1.074
<i>R</i> Indices (all data) ^{a,b}	<i>R</i> 1 = 0.0551 <i>wR</i> 2 = 0.1059	<i>R</i> 1 = 0.0531 <i>wR</i> 2 = 0.1189
Largest differential peak and hole [e/Å ³]	1.298 and -1.001	1.452 and -0.991

^a *RI* = $\sum |F_o| - |F_c| / \sum |F_o|$; ^b *wR2* = $[\sum (w(F_o^2 - F_c^2))^2 / \sum (wF_o^4)]^{1/2}$.

pane (2-Me)₂P,P(2-Me)₂ or the (py)N,N(im) ligand N-(1-methyl-1-pyridylmethylidene)-2,6-diisopropyl-aniline oligomerize ethene to a mixture of isomeric olefins [10, 15]. The contents of linear olefins is significantly higher for **4**/NaBAF (98%) than for the system containing (2-Me)₂P,P(2-Me)₂ (1-olefins < 5%) under similar reaction conditions [15, 29]. Also the maximum chain length obtained with **4** (C₃₂) is significantly higher than with the (2-Me)₂P,P(2-Me)₂ complex (C₁₆). In polymerization experiments with (py)N,N(im) several isomers for one C_{*n*} fraction were also obtained (*e.g.* nine isomers for the C₁₀-fraction) [10].

The catalyst system **4**/NaBAF was tested for ethene/CO copolymerization reactions. However, only traces of 1-olefins could be isolated which were probably formed during the initiation of the reaction, before CO was added to the autoclave. The bis(aceonitrile) complex **5** also showed no activity for the copolymerization of ethene and CO at room temperature (using methanol as cocatalyst).

Conclusion

We synthesized the P,N ligands **1** and **2** as well as several of their palladium complexes. The X-ray structure analysis of the PdI₂ complexes revealed a distorted square-planar coordination sphere for the metal atoms. In both compounds the Pd–I bond *trans* to the phosphorus atom was longer than the one *trans* to nitrogen. The chloro-methyl palladium complex of **1** was used for the oligomerization of ethene after activation with a borate salt. This system produces a mixture of isomers with a high content of linear 1-olefins. No activity for the copolymerization of ethene and CO was observed at room temperature.

Experimental Section

All manipulations except the handling of the palladium diiodide complexes were carried out in dry solvents under an argon atmosphere using standard Schlenk techniques. THF and diethyl ether were distilled from LiAlH₄; CH₂Cl₂ was distilled from CaH₂. All solvents were stored over

molecular sieves. Commercially available acetonitrile (water contents < 30 ppm), 2-(chloromethyl)pyridine hydrochloride, acetophenone, lithium diisopropylamide (THF-complex, 1.5 molar solution in cyclohexane), potassium *tert*-butanolate (95%), chlorodiphenylphosphane (95%), KCN, NaI and AgBF₄ were used without further purification. 2,6-Diisopropylaniline (techn.) was purified by distillation. (*Cis,cis*-cycloocta-1,5-diene)dichloropalladium (COD)PdCl₂ [30], (*cis,cis*-cycloocta-1,5-diene)chloromethylpalladium (COD)PdClMe [31], sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAF) [32] and bis(2-methyl-phenyl)phosphane [33] were prepared according to literature procedures. NMR measurements were conducted on a Bruker DRX 400 spectrometer. Chemical shifts are reported in ppm. Tetramethylsilane and 85% phosphoric acid were used as references. FAB-MS spectra were measured on a Finnigan MAT TSO 7000 spectrometer using 2-nitrophenyloctylether (2-NPOE) as matrix. GC-MS measurements were performed on a Varian Saturn GC/MS 2000 spectrometer. Melting points were determined on a Büchi B-540 (2 °C/min). Elemental analysis were measured on a Vario EL elementar.

2-[Bis(2-methyl-phenyl)phosphinomethyl]pyridine (**1**)

2-(Chloromethyl)pyridine (3.20 g, 25 mmol), generated from the hydrochloride using an aqueous solution of NaHCO₃, was dissolved in 50 ml of THF and the solution added to bis(2-methyl-phenyl)phosphane (5.37 g, 25 mmol) in 50 ml of THF. Potassium *tert*-butanolate (5.61 g, 50 mmol) was added and the reaction mixture was stirred at RT for 48 h. The solvent was removed under reduced pressure and the solid residue was dissolved in 100 ml of CH₂Cl₂ and 100 ml of water. The organic phase was separated and the aqueous phase extracted with 100 ml of CH₂Cl₂. The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product (87% pure according to ³¹P NMR analysis) was used without further purification. Analytical data were determined from a pure sample which was generated from the diiodide complex. – ¹H NMR (CDCl₃): 2.11 (s, 6H, *Me*), 3.44 (s, 2H, CH₂P), 6.75 (dd, 1H, *J*₁ = 7.8 Hz, *J*₂ = 0.9 Hz, Ar), 6.91 (m, 1H, Ar), 6.98 (m, 2H, Ar), 7.04–7.12 (m, 4H, Ar), 7.23–7.26 (m, 2H, Ar), 7.29 (m, 1H, Ar), 8.39 (dd, 1H, *J*₁ = 4.9 Hz, *J*₂ = 0.9 Hz, Ar). – ¹³C NMR (CDCl₃): 20.9 (d, *J* = 21.5 Hz), 37.9 (d, *J* = 16.2 Hz), 120.8 (d, *J* = 2.3 Hz),

123.6 (d, *J* = 6.0 Hz), 126.0, 128.5, 129.8 (d, *J* = 4.53), 131.4, 135.9, 136.5 (d, *J* = 15.5 Hz), 142.3 (d, *J* = 25.7 Hz), 149.3, 158.3 (d, *J* = 8.3 Hz). – ³¹P NMR (CDCl₃): –30.44.

Diiodo-{2-[bis(2-methyl-phenyl)phosphinomethyl]pyridine}palladium(II) (**3**)

(COD)PdCl₂ (7.16 g, 25 mmol) was added to a solution of **1** (7.63 g, 25 mmol) in 100 ml of CH₂Cl₂. After the solution had been stirred for 5 min NaI (15.04 g, 100 mmol) was added and the reaction mixture was stirred at RT for 48 h. After filtration the solvent was removed under reduced pressure and the product was purified by column chromatography on silica using CH₂Cl₂/petroleum ether (30:1) as eluent. Yield: 64%. M.p. 273 °C (decomp.) – ¹H NMR (CDCl₃): 2.65 (s, 6H, *Me*), 4.36 (d, 2H, *J* = 12.6 Hz, CH₂P), 7.24–7.31 (m, 5H, Ar), 7.42–7.46 (m, 3H, Ar), 7.79 (m, 1H, Ar), 7.90 (m, 2H, Ar), 10.09 (dd, 1H, *J*₁ = 5.9 Hz, *J*₂ = 1.0 Hz, Ar). – ³¹P NMR (CDCl₃): 40.95. – FAB-MS (matrix: 2-NPOE): *m/z* 665 (M⁺, 10%), 638 (M⁺–I, 60%). – Elemental analysis (C₂₀H₂₀I₂NPPd): calcd. C 36.09, H 3.03, N 2.10; found C 36.10, H 3.10, N 2.12.

{[Bis(2-methylphenyl)phosphinomethyl]pyridine}-chloromethylpalladium(II) (**4**)

3 (1 g, 1.5 mmol) and KCN (65 mg, 30 mmol) were dissolved in 10 ml of CH₂Cl₂ and 15 ml of water. After 5 min the organic phase had decolorized, but the reaction mixture was stirred over night. The aqueous phase was separated and the organic phase extracted with water (4 × 20 ml). The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure to leave the product as a colorless solid which was dried under vacuum. (COD)PdClMe (1 eq.) was added to a solution of the ligand in 20 ml of CH₂Cl₂ and the reaction mixture was stirred over night. The solvent was reduced to 5 ml and 80 ml of Et₂O was added. The colorless precipitate was separated, washed with 2 × 15 ml of Et₂O and dried under vacuum. Yield: 82%. – ¹H NMR (CDCl₃): 0.67 (d, 3H, *J* = 2.8 Hz, PdMe), 2.53 (s, 6H, *Me*), 4.14 (d, 2H, *J* = 11.1 Hz, CH₂P), 7.19 (m, 2H, Ar), 7.24–7.30 (m, 3H, Ar), 7.40 (m, 2H, Ar), 7.45 (d, 1H, *J* = 7.8 Hz, Ar), 7.59 (m, 2H, Ar), 7.74 (m, 1H, Ar), 9.43 (dd, 1H, *J*₁ = 5.4 Hz, *J*₂ = 1 Hz, Ar). – ³¹P NMR (CDCl₃): 36.6. – FAB-MS (matrix: 2-NPOE, CH₂Cl₂): *m/z* 462 (M⁺–H, 12%), 426 (M⁺–Cl, 80%), 410 (M⁺–HCl–CH₃, 100%). – Elemental analysis (C₂₁H₂₃ClNPPd): calcd. C 54.56, H 5.02, N 3.03; found C 54.58, H 5.07, N 3.00.

Bis(acetonitrile-[2-bis(2-methyl-phenyl)phosphino-methylpyridine]palladium bistetrafluoroborate (5)

AgBF₄ (607 mg, 3.12 mmol) was added to a suspension of **3** (1.04 g, 1.56 mmol) in 50 ml of acetonitrile. The reaction mixture was stirred at RT over night and filtered, and the solvent was removed under reduced pressure. The solid residue was extracted with CH₂Cl₂ (2 × 20 ml). Removal of the solvent left the product as a pale yellow, microcrystalline solid. Yield: 98%. – IR (KI-pellets): 2334, 2307 (N≡C–CH₃, m), 1075 (BF₄[–], bs). – ¹H NMR (CDCl₃): 2.17 (s, 3H, NCMe), 2.39 (s, 3H, NCMe), 2.62 (s, 6H, Me), 4.66 (d, 2H, *J* = 14.0 Hz, CH₂P), 7.40–7.48 (m, 4H, Ar), 7.57 (dd, 1H, Ar), 7.67 (m, 2H, Ar), 7.80–7.90 (m, 3H, Ar), 8.05 (m, 1H, Ar), 8.67 (d, 1H, *J* = 6.0 Hz, Ar). – ³¹P NMR (CDCl₃): 51.54. – FAB-MS (matrix: 2-NPOE): *m/z* 411 (M²⁺–2CH₃CN–2BF₄, 100%).

N-(1-phenylethylidene)-2,6-diisopropyl-aniline

A solution of acetophenone (24.7 ml, 0.2 mol), 2,6-diisopropyl-aniline (40 ml, 0.21 mol), formic acid (10 ml) and 200 ml of methanol was stirred at RT for 48 h. Upon reduction of the volume of the solvent the crude product precipitated and was further purified by column chromatography on silica using CH₂Cl₂/petroleum ether (6:1) as eluent. Yield: 25%. – ¹H NMR (CDCl₃): 1.13 (d, 6H, *J* = 5.3 Hz, CHMe), 1.15 (d, 6H, *J* = 5.0 Hz, CHMe), 2.09 (s, 3H, Me), 2.75 (sep, 2H, CHMe), 7.07 (m, 1H, Ar), 7.13 (s, 1H, Ar), 7.15 (s, 1H, Ar), 7.48 (m, 3H, Ar), 8.03 (m, 2H, Ar). – ¹³C NMR (CDCl₃): 17.9, 22.8, 23.1, 28.1, 122.8, 123.1, 127.0, 128.2, 130.2, 135.9, 139.0, 146.6, 164.6; EI-MS *m/z* 279 (M⁺, 30%), 264 (M⁺–CH₃, 100%).

N-[2-(Diphenylphosphino)-1-phenylethylidene]-2,6-diisopropyl-aniline (2)

Lithium diisopropylamide (6.6 mmol) was added slowly to a solution of N-(1-phenylethylidene)-2,6-diisopropyl-aniline (1.6 g, 5.7 mmol) in 100 ml of diethyl ether at –78 °C. After chlorodiphenylphosphane (1.1 ml, 5.7 mmol) had been added the reaction mixture was allowed to reach RT and was stirred for additional 2 h. Evaporation of the solvent left the crude product in about 65% yield (according to ³¹P- and ¹H NMR analysis). The product was used without further purification.

Diiido-{N-[(Z)-2-(diphenylphosphine)-1-phenylethylidene]-2,6-diisopropyl-aniline}palladium(II) (6)

(COD)PdCl₂ (1 equiv.) was added to a solution of the ligand in 200 ml of CH₂Cl₂. After 5 min NaI

(4 equiv.) was added and the reaction mixture was stirred over night and filtered, and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica using CH₂Cl₂/EtAc (100:1) as eluent. The complex proved to be unstable in solution (halogenated solvents). – ¹H NMR (CD₂Cl₂): 0.28 (d, 6H, *J* = 6.7 Hz, CHMe), 1.29 (d, 6H, *J* = 6.7 Hz, CHMe), 2.77 (sep, 2H, *J* = 6.7 Hz, CHMe), 4.38 (d, 2H, *J* = 13.4 Hz, CHMe), 6.94 (m, 4H, Ar), 7.11 (m, 3H, Ar), 7.28 (t, 1H, *J* = 7.4 Hz, Ar), 7.45–7.57 (m, 6H, Ar), 7.76 (m, 4H, Ar). – ³¹P NMR (CD₂Cl₂): 41.66. – FAB-MS (matrix: 2-NPOE, DMF) *m/z* 823 (M⁺, 5%), 696 (M⁺–I, 100%) elemental analysis (C₃₂H₃₄I₂NPPd): calcd. C 46.65, H 4.16, N 1.70; found: C 45.94, H 4.09, N 1.72.

Polymerizations

Polymerization experiments were performed in an 100 ml steel autoclave (Roth) with a glass inlet and mechanical stirring. Ethene (BASF, 2.7) was used without further purification. The autoclave was purged with argon prior to use. Under an inert atmosphere **4** (50 μmol) and NaBAF (50 μmol) were stirred in 10 ml of diethyl ether for 10 min. The solid residue was removed by filtration and the solution was transferred to the autoclave which had been charged with 30 ml of CH₂Cl₂. The autoclave was pressurized with ethene for 5 min. The reaction was quenched by the addition of water after 1 h. The reaction mixture was analyzed by GC-MS.

Crystallography

Crystal data of the compounds **3** and **6** were collected with a Rigaku AFC7S single-crystal diffractometer at 193(2) K using Mo–K_α radiation (graphite monochromator), λ = 0.71073 Å (ω/2-θ-scans). Intensities were corrected for Lorentz and polarization effects [34]. A ψ-scan absorption correction was performed, 0.75 < T < 1.00 (**3**), 0.573 < T < 1.000 (**6**) [35]. Solution and refinement: SHELX-97 (Sheldrick, 1997); figures with the labelling scheme: ORTEP3 (Farrugia, 1997) [36]. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions. The displacement factor of the H-atoms was 1.2× (or 1.5× for methyl hydrogens) that of the host atom.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 179852 for compound **3**, CCDC 179853 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cam-

bridge, CB2 1EZ UK, Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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