

Two-phase hydroformylation reaction catalysed by rhodium-complexed water-soluble dendrimers[☆]

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Abstract

Four water-soluble dendritic phosphonated ligands were first synthesized based on poly(amidoamine) (PAMAM) (generation 3 with 32 cascade end groups), with the hydrophilic amine or sulfonic acid groups on the surface of the dendrimer. Their Rh(I) complexes were used as the catalysts in the two-phase hydroformylation of styrene and 1-octene at mild reaction conditions. The results showed that these new water-soluble dendritic catalysts exhibited high catalytic activity both for 1-octene and styrene. These new catalysts also exhibited high selectivity for the iso-aromatic aldehyde, while in the long chain olefin case the selectivity was benefited for normal aldehyde. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Dendrimer; Water-soluble ligand; Two-phase hydroformylation

1. Introduction

Though the aqueous biphasic catalysis system is already the subject of comprehensive reports, and more than 10 years has passed after the unrivalled introduction of trisodium tris(*m*-sulfanotophenyl) (TPPTS) as a water-soluble ligand of aqueous catalysis in industry [1–3], this subject is still established as one of the most promising areas in homogeneous catalysis now. Especially, the biphasic hydroformylation catalysed by water-soluble phosphine ligands complexed with rhodium have attracted much

attention [4–14]. One advantage of this two-phase system is that it resolved the basic problem of homogeneously catalysed process, i.e. the separation of product phase from the catalyst, thus the catalyst can be re-used to save the precious metal. Taking water as one phase in the two-phase method brings to another apparent benefit, i.e. the ubiquitousness, lack of odour and non-flammability of water, which make it suitable for environmental and safety reasons for industrial applications. But owing to the fact that the hydrophilic catalyst, which is insoluble in the organic product phase, brings about the catalytic reactions in the aqueous phase or at the phase boundary, the reaction rate in the two-phase system is mainly determined by the solubility of olefins in water. Usually, the results of olefins with long chains were not satisfied, because its solubility in aqueous phase is poor. In

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order to improve the reaction speed and selectivity of hydroformylation, new water-soluble ligands are expected.

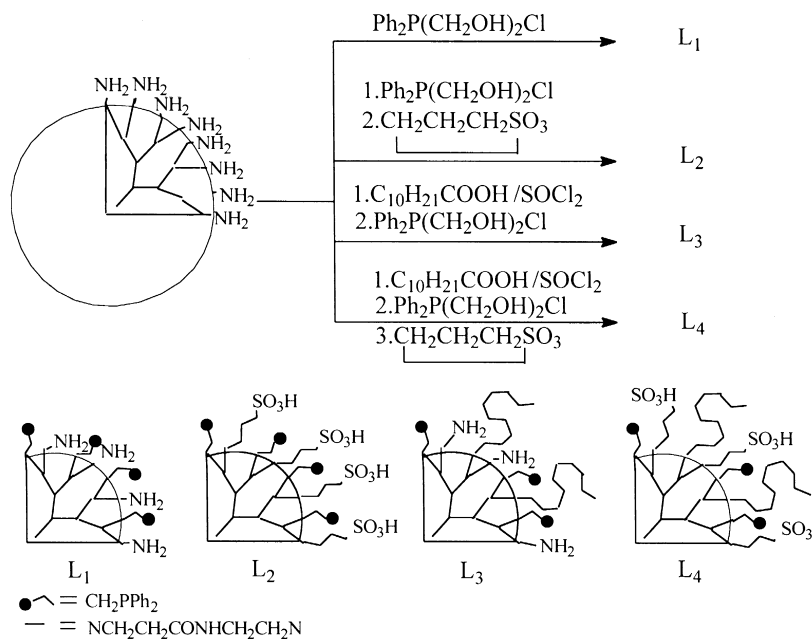
Dendrimers, the highly branched macromolecules with globular outlook, voids inner and multiple reactive sites on the molecular surface and have already shown their potential use as catalysts [15–20] or auxiliary [21–23] in organic chemistry, biochemistry and polymer science etc. In 1997, Reetz et al. used a polyaminodiphosphine dendrimer as support for rhodium and palladium catalyst [20]. Very recently, Bourque et al. have developed heterogeneous polyamidoamino diphosphonated dendrimers built on a silica gel core support ($\text{PPh}_2\text{-PAMAM-SiO}_2$) [24]. They observed that these dendrimers, when complexed to Rh(I), are excellent catalysts for the hydroformylation reaction. To our best knowledge, study on two-phase hydroformylation catalyzed by water-soluble dendritic catalyst has not been reported. In this paper, the typical water-soluble dendrimer, poly(amidoamine) (PAMAM) generation 3.0 with 32 cascade end amine groups (G_3) was chosen as support. By its reaction with

$\text{PPh}_2(\text{CH}_2\text{OH})_2\text{Cl}$, dendritic ligands containing phosphine on PAMAM molecular surface (Scheme 1) have been prepared. Their Rh(I) complex catalysts showed high selectivity for branched aromatic aldehyde and good yields in the hydroformylation reaction of styrene and 1-octene under mild reaction conditions.

2. Experimental

All reactions were done under an inert atmosphere. *n*-undecylic acid (> 97%) and 1-octene (> 97%) was obtained commercially and was used directly. Styrene was distilled prior to use. $\text{Rh}(\text{CO})_2(\text{acac})$ and 1,3-propane sultone (> 97%, ACROS) was obtained commercially. $\text{PPh}_2(\text{CH}_2\text{OH})_2\text{Cl}$ was prepared according to Ref. [25]. PAMAM G_3 (molecular weight = 6909) was synthesized according to literature [26]. All reagents and solvent were distilled and stored in a 4-Å molecular sieve before use.

FT-IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. ^1H NMR and ^{31}P NMR were carried on a Varian



Scheme 1. Segment of the globular structure of water-soluble dendritic ligands $\text{L}_1\text{-L}_4$.

300 MHz spectrometer in CDCl_3 and CD_3OH , respectively. TMS was used as standard for ^1H NMR and 85% H_3PO_4 for ^{31}P NMR, giving positive values down field. Elemental analyser Carlo Erba 1106 and ST02 performed elemental analysis. Atomic absorption analysis was carried out on a Perkin-Elmer 5000 spectrometer.

2.1. Preparation of the water-soluble dendritic ligands

Dendritic PAMAM G_3 was chosen as the support, which was partially phosphonated on the surface by its reaction with $\text{PPh}_2(\text{CH}_2\text{OH})_2\text{-Cl}$ to give dendritic phosphine ligand L_1 (as shown in Scheme 1).

By controlling the amount of hydrophobic and hydrophilic reactant, ligand L_1 can be prepared in a large scale and has a good solubility in water. But much more hydrophobic phosphine groups would reduce the water solubility of the ligand. In order to load more phosphine groups on the surface of the dendrimer while maintaining good solubility in water, the hydrophilic 1,3-propane sultone was introduced, and then the phosphonated PAMAM ligand L_2 was synthesized by the reaction of G_3 with more $\text{PPh}_2(\text{CH}_2\text{OH})_2\text{Cl}$, then followed by reaction with 1,3-propane sultone. For comparison purposes, another two phosphonated PAMAM ligands (L_3 and L_4) were synthesized, in which several aliphatic long chains were introduced on the surface of the dendrimer by the reaction of G_3 with *n*-undecylic acid chloride. These two dendritic phosphine ligands bearing hydrophobic long aliphatic chains were expected to enhance the solubility of olefins in water, which could result in improvement of the reaction rate. All the phosphonated dendrimers were obtained as pale yellow powder and characterized by ^1H NMR, ^{31}P NMR and FT-IR (as shown in Table 1).

A typical preparation of L_4 was shown as follows: 1.78 g *n*-undecylic acid was dissolved in 20 ml CH_2Cl_2 in a 50 ml three-neck flask, 0.8 ml SOCl_2 and 1.8 ml pyridine were added.

The mixture was stirred at room temperature for 4 h, then the reaction solution was dropped into a 250-ml three-neck flask equipped with a magnetic stir bar and charged with 70 ml methanol solution of 2 g (0.29 mmol) G_3 and 3 ml triethylamine. Under the protection of nitrogen, the reaction solution was stirred at ambient temperature for 24 h. After concentration, the reaction product was precipitated out by a mixed-precipitant of petroleum ether/ethyl acetate (100 ml/100 ml), then the solid was dissolved in methanol (10 ml) and re-precipitated first by petroleum benzine/ethyl acetate, and then twice by chloroform/ethyl acetate, respectively. After filtration and drying in vacuum for 48 h, 2.36 g yellow solid precursor was obtained.

A 100-ml three-neck flask containing 0.7 g (2.03 mmol NH_2) precursor prepared above and 0.29 g (1.02 mmol) $\text{PPh}_2(\text{CH}_2\text{OH})_2\text{Cl}$ was purged with nitrogen for 30 min, then 25 ml methanol was added by a syringe. After the solid was dissolved completely, 0.17 ml triethylamine was injected by a syringe. The mixture was stirred at ambient temperature for 45 min, then at refluxing temperature for 2 h. The mixture was allowed to be stirred at room temperature overnight. After that, 5 ml methanol solution of 0.37 g (3.05 mmol) 1,3-propane sultone was added under nitrogen, and the reaction mixture was stirred for another 24 h. After concentration, the reaction solution was precipitated in a light yellow solid with a mixed-precipitant of petroleum benzine/ethyl acetate (100 ml/100 ml) to give a light yellow solid. After re-precipitation, the solid was washed with ethyl ether (20 ml \times 3) and dried in vacuum for 48 h at room temperature. A 0.76 g product L_4 was obtained.

2.2. The complex style of rhodium with the dendritic ligands

In the preparation of the dendritic ligands by the reaction of PAMAM or its modification product containing aliphatic long chain with $\text{PPh}_2(\text{CH}_2\text{OH})_2\text{Cl}$, the mole ratio of feed

Table 1
The characterization of L₁, L₂, L₃ and L₄

Run	L ₁	L ₂	L ₃	L ₄
M_w^a	8692	13 896	9063	11 649
P(III) ^a	9 ^b	18 ^b	4 ^b	6 ^b
n^a	–	–	8	8
³¹ P NMR (ppm)	–20.0, –27.4 ^c	–24.0, –28.2 ^c	–20.9, –23.0, –23.2, –26.5, –27.4 ^c	–20.9, –22.9, –23.1, –26.4, –27.3 ^c
¹ H NMR (D ₂ O) (ppm)	7.50, 3.32, 3.16, 2.93, 2.69, 2.58, 2.32	7.70, 7.84, 3.57, 3.32, 3.19, 2.99, 2.54, 2.15	7.63, 7.20, 3.73, 3.20, 1.00, 0.71	7.79, 7.72, 7.19, 3.57, 3.45, 3.32, 3.11, 2.81, 1.01
FT-IR (KBr) (cm ⁻¹)	NH: 3421.69, 3279.44; CH ₂ : 2963.61, 2831.31; CO: 1646.95, 1551.10; Ph: 1459.33, 1436.58 Ph: 1459.33, 1436.58	NH: 3445.31, 3297.77; CH ₂ : 2948.21, 2837.01; CO: 1644.46, 1552.73; Ph: 1460.84, 1438.86; SO ₃ H: 1199.28, 1041.82	NH: 3423.45, 3281.10; CH ₂ : 2927.10, 2855.06; CO: 1657.32, 1552.51; Ph: 1460.10, 1437.42	NH: 3423.29, 3271.84; CH ₂ : 2927.38, 2855.24; CO: 1657.63, 1553.46; Ph: 1459.83, 1438.41; SO ₃ H: 1189.90, 1040.73

^aDetermined by ¹H NMR and ³¹P NMR; n : the number of long aliphatic chain.

^bThe number of P(III) per ligand molecule.

^cThe peak was very weak.

amount of $\text{PPh}_2(\text{CH}_2\text{OH})_2\text{Cl}$ to NH_2 group was controlled to be 1:2 or 1:3. From these reaction ratios, it was suggested that the NH_2 group had not completely been reacted, which meant that monodentate phosphine ($-\text{NHCH}_2\text{-PPh}_2$) might be the main group on the surface of the dendrimer. This complex style was proved further by ^{31}P NMR (in D_2O) analysis, and L_2 was taken as the typical model, its chemical shifts were -24 (strong peak) and -28 ppm (weak peak) for uncomplexed L_2 . Comparing with the result of ^{31}P solid-state NMR (uncomplexed $\delta = -27$ to -28 ppm) for the diphosphonated amino group of PAMAM which acts as a bidentate ligand for the hydroformylation [10], the chemical shifts of -24 ppm for uncomplexed L_2 could not be attributed to the ligand with diphosphonated amino group. Accordingly, we thought that the main chemical shift of -24 ppm for L_2 was attributed to the monophosphonated amino group in our experiment, and -28 ppm was contributed to biphosphonated amino group, that is the phosphonated ligands used in our work were mainly monophosphonated amino ligand besides a little biphosphonated amino ligand.

2.3. Two-phase hydroformylation in the autoclave

In order to assess the efficiency of the new dendritic phosphine ligands in two-phase catalytic hydroformylation reaction, styrene and 1-octene were chosen as the typical substrates. The reason for this choice was based on the following facts. First, styrene is a representative of aromatic substrates, and in the fine chemistry view the aromatic aldehyde is a useful material in industry. Second, 1-octene is a representative substrate of heavy olefins whose solubility in water is poor in the two-phase hydroformylation. Here toluene was chosen as the organic solvent and the dendritic complex of Rh(I)-L was prepared in situ. For a typical reaction, 8.97 mg L_2 (0.012 mmol P) and 1 mg $[\text{Rh}(\text{CO})_2(\text{acac})]$ (3.87×10^{-3} mmol) were dis-

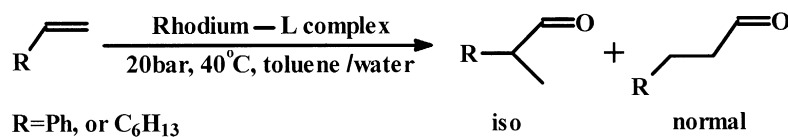
solved in 1.5 ml toluene and 1.5 ml water, corresponding to a Rh/P ratio of 1:3 (the amount ligand added is dependent on the selected Rh/P ratio). The resulting biphasic mixture was stirred till the organic phase was colourless, and then 0.1 ml styrene (0.87 mmol or 0.1 ml 1-octene, 0.57 mmol) was added. The autoclave was pressed and vented three times with CO and the pressure was set to 20 bar ($\text{CO}/\text{H}_2 = 1:1$). The autoclave was heated to 40°C by oil bath and the reaction commenced by starting the stirring. After the reaction, the autoclave was cooled to room temperature and depressurized. The organic phase was separated and immediately analyzed with GC and ^1H NMR. The selectivity of aldehyde was more than 99% in all the cases.

3. Results and discussion

3.1. Hydroformylation of olefins catalysed with rhodium-complexed water-soluble dendrimers

In our present work, this kind of water-soluble ligands containing phosphines was obtained with mostly monophosphonated amino groups on their globular molecular surface, according to the reactant molar ratio that $\text{PPh}_2(\text{CH}_2\text{OH})_2\text{Cl}$ was 1:2 or 1:3 equivalent to NH_2 group. The catalytic activity of rhodium-complexed phosphino PAMAM dendrimers was investigated with regards to the hydroformylation reaction as follows, where styrene and 1-octene were taken as typical substrates (Scheme 2).

In general, the products of hydroformylation of styrene catalyzed with Rh(I) complexed with the typical diphenyl phosphino ligands such as TPPTS, BISBIS-Na (disodium salt of bis disulfonato diphenylphosphinomethyl disulfonato biphenyl), NORBOS-Na (trisodium salt of tris trisulfonatophenyl dimethyl phosphanobornadiene), BINAS-Na (tetrasodium salt of bis disulfonato diphenylphosphinomethyl tetrasulfonato binaphthene) etc. [7] were mostly normal aldehyde [6]. However, from the fine chemistry



Scheme 2. The equation of the hydroformylation of styrene and 1-octene.

viewpoint, the iso-aldehydes are more important as they provide valuable intermediates for the pharmaceutical industry. In our case, where the phosphonated PAMAM dendrimers were taken as the catalyst ligands in hydroformylation of styrene, the products were almost branched as aromatic aldehyde at 40°C (see Table 2). In entry 2, the ratio of iso-aldehyde (i) to normal aldehyde (n) was 15:1; compared to the product of TPPTS whose i/n ratio was 6:94 [7], the branched aldehyde catalyzed by rhodium- L_1 was high. By changing the amount of ligand, it was found that the reaction speed and the selectivity of the hydroformylation of styrene were changed correspondingly. The more the amount of the ligand, the higher the selectivity for iso-aromatic aldehyde and the lower the reaction speed. When the ratio of palladium to rhodium was increased to 11:1 for L_2 , the ratio of i/n reached 29:1.

In the case of 1-octene, the reaction phenomenon was the same as that of styrene except that the selectivity of the complex of rhodium- L for iso-aldehyde was poor. Though the ratio of i/n was only 1:2 for entry 11 (see Table 3), it was still higher than TPPTS [10]. Besides, the reaction speed of 1-octene catalyzed by the rhodium- L was high, and the yield of aldehyde was more than 70% for L_1 .

In order to explain the experimental phenomenon, two other comparable experiments were done. In one case, the same reaction condition as that for entry 4 was taken except that the phosphonated ligands was replaced with G_3 . The result was that no aldehyde was produced at all. In the other case, with the same reaction condition but having no ligand and only Rh(I) as the catalyst, the reaction speed was the highest in all the cases with a very poor selectivity for iso-aliphatic aldehyde; the ratio of i/n was only 4:1.

In order to explore the effect of dendritic ligand on the leaching of Rh in the samples, we took the organic phase of entry 17, 18, 19 as samples for atomic absorption measurement. The results showed that after the hydroformylation reaction, the Rh leaching in organic phase was 3.60% (w%) for entry 17 ($P/Rh = 2$), 1.86% (w%) for entry 18 ($P/Rh = 3$) and 1.02% (w%) for entry 19 ($P/Rh = 4$), respectively. It is obvious that the presence of more ligands is beneficial for diminishing the leaching of metal.

Until now, it was clear that the amount of the dendritic ligand took an important role on the catalytic activity and selectivity, as well as the leaching of metal. The detailed results were listed in Tables 2 and 3.

Table 2
The hydroformylation of styrene with different ratios of ligand^a

Entry	Ligand	Substrate	P/Rh	Time (h)	Yield (%)	i/n	TON (h^{-1})	Colour (organic phase)
1	L_1	styrene	3	16	49	14:1	6.90	light yellow
2	L_1	styrene	6	12	21	15:1	4.00	light yellow
3	L_2	styrene	3	16	63	11:1	8.85	light yellow
4	L_2	styrene	11	16	59	29:1	8.36	light yellow
5	L_3	styrene	3	16	49	23:1	6.82	light yellow
6	L_3	styrene	6	16	0	–	–	colourless
7	L_4	styrene	1	16	75	12:1	10.53	yellow
8	L_4	styrene	3	16	56	18:1	7.88	light yellow
9	L_4	styrene	4	16	6	26:1	0.83	colourless

^aCO/H₂ = 1:1 (20 bar); 40°C; reactive solution: toluene/water = 1.5:1.5 ml.

Table 3
The hydroformylation of 1-octene with different ratios of ligand^a

Entry	Ligand	Substrate	P/Rh	Time (h)	Yield (%)	i/n	TON (h ⁻¹)	Colour (organic phase)
10	L ₁	1-octene	3	20	78	1:2.3	5.73	light yellow
11	L ₁	1-octene	6	18	70	1:2.0	5.75	light yellow
12	L ₂	1-octene	3	4	67	1:2.1	24.57	light yellow
13	L ₂	1-octene	11	25	30	1:2.5	1.75	light yellow
14	L ₃	1-octene	2	12	82	1:3.2	10.06	yellow
15	L ₃	1-octene	3	20	19	1:1.5	1.43	light yellow
16	L ₃	1-octene	6	20	0	–	–	colourless
17	L ₄	1-octene	2	12	49	1:4.2	6.05	yellow
18	L ₄	1-octene	3	20	15	1:1.5	1.13	light yellow
19	L ₄	1-octene	4	20	13	1:1.3	0.93	colourless

^aCO/H₂ = 1:1 (20 bar); 40°C; reactive solution: toluene/water = 1.5 ml.

When the ratio of P/Rh was lower, for example entry 7 or 14, the organic phase product was yellow, the yield of aldehyde was high and the selectivity was poor, which could be owed to the uncomplexed or leaching of noble metal. When the ratio of P/Rh was as high, such as entry 4 or 11, lower yield of aldehyde and higher selectivity for iso-aldehyde were obtained. The organic phase was light or colourless, which was attributed to the less leaching of metal and the possible existence of the complex Rh(I) with NH₂ end group.

3.2. The effect of temperature on the hydroformylation of olefin

After hydroformylation, the colour of the organic phase was light yellow at 40°C. When the reaction temperature rose to 60°C, the reaction speed of the hydroformylation was improved, but the selectivity for branched aromatic aldehyde was decreased, and the colour of the organic solution became much deeper, suggesting that some more leaching of the rhodium metal occurs. This leaching was found to be less

Table 4
Hydroformylation of styrene and 1-octene catalysed by Rh(I) complexed with L₁, L₂, L₃, and L₄

Entry	Ligand	Substrate	Rh/olefin	Time (h)	Yield (%)	i/n	TON (h ⁻¹)
20	L ₁	styrene	1:225 ^a	16	49	14:1	6.90
21	L ₁	styrene	1:225 ^b	16	100	12:1	> 14.1
22	L ₁	1-octene	1:147 ^a	20	78	1:2.3	5.73
23	L ₁	1-octene	1:147 ^b	10	100	1:2.0	> 14.7
24	L ₂	styrene	1:225 ^a	16	63	12:1	8.85
25	L ₂	styrene	1:225 ^b	16	100	10:1	> 14.1
26	L ₂	1-octene	1:147 ^a	4	67	1:2.1	24.6
27	L ₂	1-octene	1:147 ^b	10	100	1:2	> 14.7
28	L ₃	styrene	1:225 ^a	16	49	23:1	6.82
29	L ₃	styrene	1:225 ^b	16	82	21:1	11.6
30	L ₃	1-octene	1:147 ^a	20	19	1:1.5	1.43
31	L ₃	1-octene	1:147 ^b	20	49	1:1.2	3.58
32	L ₄	styrene	1:225 ^a	16	56	18:1	7.88
33	L ₄	styrene	1:225 ^b	16	72	16:1	10.2
34	L ₄	1-octene	1:147 ^a	20	15	1:1.6	1.13
35	L ₄	1-octene	1:147 ^b	20	57	1:1.5	4.18

20 bar, CO/H₂ = 1:1, Rh/P = 1:3.

^a40°C

^b60°C

evident when the ratio of phosphine to rhodium increased further, but the selectivity for branched aldehyde decreased (Table 4). In contrast with the styrene, the main product of hydroformylation from 1-octene was normal aldehyde, and the selectivity was not so satisfied as described above. When raising the reaction temperature to 60°C, the selectivity for the branched aldehyde further increased for 1-octene, and the activity of the catalyst also increased.

3.3. The effect of ligands with long aliphatic chain on two-phase hydroformylation reaction

As can be seen from Table 4, once water-soluble dendritic ligand was added, the selectivity for branched aldehyde increased for the styrene products, and the yield of iso-aldehyde in all these products can reach over 90% (see Table 4, entries 20, 21, 24, 25, 28, 29, 32 and 33). In order to understand better the effect of ligands with long aliphatic chain on the catalytic activity, entries 22, 26, 30 and 34 were taken as models (see Table 4). Comparing the models with L_1 and L_2 , L_3 and L_4 , which are with long aliphatic chain on their molecular surface, seemed to reduce the catalytic activity evidently. One reason is thought to be the less phosphine groups on the surface (see Table 1); the other reason might be that the long chain acted as a steric hindrance, which resisted the complex of Rh(I) with L.

4. Conclusion

The four novel water-soluble phosphonated dendritic ligands were prepared based on the PAMAM dendrimer and were mainly monophosphonated amino ligands. Their Rh(I) complexes exhibited a high selectivity for the iso-aldehyde formation in the hydroformylation of styrene. Though the selectivity for the hydroformylation of 1-octene was not so good as that

for styrene, the reaction speed catalysed by the complex of L_1 or L_2 with rhodium was high. The increase of the ratio of the ligand to rhodium would decrease the reaction speed.

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