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Highly efficient and recyclable water-soluble fullerene-supported PdCl$_2$ nanocatalyst in Suzuki–Miyaura cross-coupling reaction

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A water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C$_{60}$-TEG$_5$/PdCl$_2$] was prepared by coordination of water-soluble fullerene nanoparticles with palladium chloride. In pure water, the catalytic activity of nanocatalyst [C$_{60}$-TEG$_5$/PdCl$_2$] for Suzuki–Miyaura cross-coupling reaction was investigated under different reaction conditions. The results showed that biphenyl compounds could be synthesized in high yields at room temperature using 0.01 mol% of [C$_{60}$-TEG$_5$/PdCl$_2$] as the catalyst and K$_2$CO$_3$ as the base with the reaction time of 4 h. The catalyst was recycled five times, and the yield clearly did not decrease.

Introduction

The Suzuki–Miyaura cross-coupling reaction for aryl–aryl bond construction has been one of the most useful and convenient pathways to synthesize biphenyl complexes.[1–6] It is applied for organic functional materials and extensively employed in the synthesis of herbicides, pharmaceuticals, and natural products as biaryl motifs.[7–11] The catalyst used in the Suzuki–Miyaura cross-coupling reaction is vital for this reaction, and the search for a suitable catalyst is the latest and most challenging research area. Although nickel,[12,13] copper,[14,15] and other transition metal compounds catalyze the Suzuki–Miyaura cross-coupling reaction, palladium catalysts are employed widely. As is well-known, the rapid increase in studies about the phosphine ligand/palladium catalyst for this reaction is primarily due to its excellent donor capability and stability effect; however, its shortcomings, such as high toxicity and air- and moisture-sensitivities seriously restrict its actual applications. Therefore, phosphine-free ligands have become the focus of scientific researchers.

In recent years, many reports have shown that phosphine-free ligands of palladium are capable of activating aryl halide with phenylboronic acid for the Suzuki–Miyaura cross-coupling reaction. Among these, phosphine-free ligands, *N*-phenylurea,[16] *N*-heterocyclic carbine,[17] isoxazol-3-amine[18] and other bis(-thiourea) species[19] exhibit high catalytic activities and stabilities. However, some problems such as lack of coordination flexibility, difficulty in synthesis, use of toxic reagent, and relatively harsh experimental conditions still need to be solved.

To resolve the above-mentioned challenges, it was necessary to find a new type of catalyst. Compared to many of the mentioned catalysts, supported catalysts used in Suzuki–

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Miyaura cross-coupling reaction with good coordination ability, easy synthesis, cost-effectiveness, and high thermal stability have become the core research focus of scientific researchers.[20–25] A number of studies have been reported for the immobilization of palladium nanocatalysts on support materials such as polyvinyl pyrrolidone[26] (PVP), amphiphilic resin,[27] *N*,*N*-dihexylcarbodiimide,[28] silica gel,[29] and PEG-2000 (ref. 30–33) and by using them, high yield can mostly be obtained. It has been verified that coordination bonding catalytic active substances with high surface energies and high surface-to-volume ratios can improve supported catalysts' efficiency.[34,35] However, there are still some problems with the supported catalyst. For example, the recyclability of PdCl$_2$ immobilized on polyacrylamide was limited because Pd^{II} is leached, leaving only the base polymer on the surface after six runs.[36]

In this study, a highly efficient and recyclable water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C$_{60}$-TEGs/PdCl$_2$] was prepared by coordination of water-soluble fullerene nanoparticles with palladium chloride. The catalytic system of [C$_{60}$-TEGs/PdCl$_2$] exhibited high activity in the Suzuki–Miyaura cross-coupling reaction of aryl bromides with aryl boronic acids at room temperature in deionized water under ambient atmosphere. In this reaction, deionized water was used as a green solvent, which was in accordance with the concept of "green chemistry". Furthermore, the [C$_{60}$-TEGs/PdCl$_2$] catalyst could be readily recovered and reused up to five consecutive runs without significant loss in its catalytic activity. As a new type of Pd nanocatalyst, the [C$_{60}$-TEGs/PdCl$_2$] catalyst was stable enough, and only small amounts of Pd were leached in a long-term static state.

Results and discussion

Characterization of [C$_{60}$-TEGs/PdCl$_2$]

At room temperature, C$_{60}$-TEGs and C$_{60}$-TEGs/PdCl$_2$ aqueous solutions were uniformly dispersed by ultrasonication and filtered

with 0.45 μm filter membranes. Their particle sizes and distributions were measured at a wavelength of 633 nm by dynamic light scattering (DLS). The average particle sizes of C_{60}-TEGs and C_{60}-TEGs/PdCl$_2$ were 42.5 nm and 61.5 nm, respectively. The TEM image of water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C_{60}-TEGs/PdCl$_2$] is shown in Fig. 1. The catalyst is spherical, and the particle size is from 30 to 90 nm. Compared with C_{60}-TEGs, [C_{60}-TEGs/PdCl$_2$] has a larger average diameter. These results indicate changes in the particle sizes or distributions of the two samples; the palladium ion within the pentacyclic structure plays a significant role in determining the particle size.

The different components of Pd 3d photoelectron peaks of nanocatalyst [C_{60}-TEGs/PdCl$_2$] are shown in Fig. 2. The peaks at 337.02 and 342.22 eV for different chemical environments of palladium confirmed the oxidation state of Pd^{2+}. PdCl$_2$ showed pi-interactions with C_{60} double bonds, and the charge transfer occurred from Pd atoms to the interstitial C atoms of C_{60}, which led to the decreasing electron density of Pd$_{3d}$.[37] However, the binding energy of Pd^{2+} did not change. From the above-mentioned results, it can be seen that PdCl$_2$ is co-ordinated to TEG to form the water-soluble fullerene-supported PdCl$_2$ nanocatalyst.

The Pd content of the catalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Table 1 shows the quantities of PdCl$_2$ and C_{60}-TEGs employed in each reaction. The coordination loading rate did not sharply increase as the amount of C_{60}-TEGs increased. Therefore, when the mass ratio of C_{60}-TEGs and PdCl$_2$ was 1 : 1, the optimum value was obtained.

Catalytic studies

To examine the catalytic activity of the water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C_{60}-TEGs/PdCl$_2$], Suzuki–Miyaura cross-coupling reaction of 4-bromoacetophenone with phenyl-boronic acid was chosen as a model reaction. The initial investigations of 4-bromoacetophenone with phenylboronic acid catalyzed by [C_{60}-TEGs/PdCl$_2$] were conducted with various conditions such as the amount of the nanocatalyst [C_{60}-TEGs/PdCl$_2$], reaction time, and different bases. As shown in Table 2, the effect of the amount of the nanocatalyst [C_{60}-TEGs/PdCl$_2$] on the coupling reaction was studied. We found that lowering the amount of [C_{60}-TEGs/PdCl$_2$] from 0.1 mol% to 0.01 mol% did not affect the
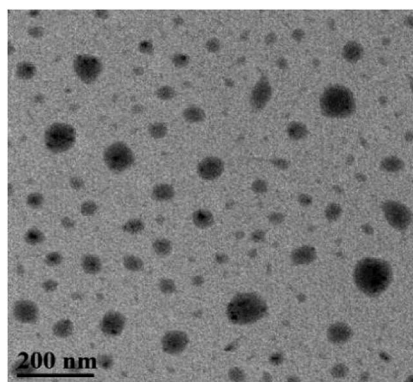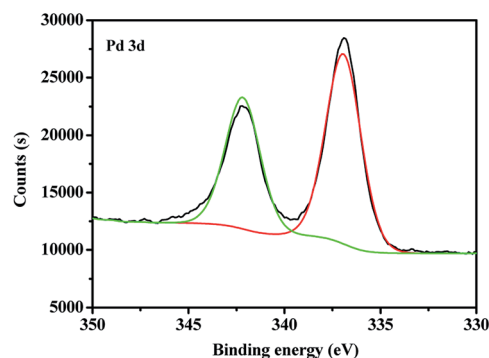

Fig. 2 Pd 3d level spectra of [C_{60}-TEGs/PdCl$_2$].

reaction performance for 2 h (entries 1–4, Table 2). When the amount of [C_{60}-TEGs/PdCl$_2$] decreased to 0.005 mol%, the reaction yield showed a sharp decline (entry 5, Table 2). The reaction time was also investigated, and it was found that it had a significant effect on the coupling reaction. After increasing the reaction time from 1 h to 4 h (entries 4, 6–8, Table 2), the yield improved remarkably. When the reaction time was prolonged to 6 h, the yield barely increased (entry 9, Table 2), because the substrate was completely converted to the product in 4 h. Furthermore, an investigation of the influence of the base suggested that the common and inexpensive inorganic bases can be used. It was found that K$_2$CO$_3$ was the best base for a high yield, whereas other bases such as Na$_2$CO$_3$, NaHCO$_3$, KF, and K$_3$PO$_4$ gave slightly lower yields (entries 10–13, Table 1). Therefore, 0.01 mol% of the catalyst, 4 h of reaction time and 2.0 mmol of K$_2$CO$_3$ as the base were considered to be the most effective conditions.

For comparison, the cross-coupling reaction of 4-bromoacetophenone and phenylboronic acid was also performed using PdCl$_2$ alone and the physical mixture of PdCl$_2$ and C_{60}-TEGS under the above-mentioned effective conditions. Using PdCl$_2$ alone, only 18% yield of product was produced in the presence of 0.01 mol% of PdCl$_2$ (entry 14, Table 2). However, in the presence of the physical mixture of PdCl$_2$ and C_{60}-TEGS, the yield of the product significantly increased to 56% (entry 15, Table 2). At identical conditions, the [C_{60}-TEGs/PdCl$_2$] nanocatalyst exhibited the highest catalytic activity. It was found that the reactivity and stability of the metal catalysts increased by the use of increasing amounts of efficacious supporting ligands.
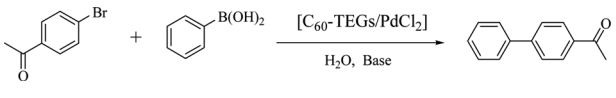
Recycling of catalyst

The recycling of water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C_{60}-TEGs/PdCl$_2$] is one of the crucial advantages of this study, which is a vital requirement for any practical application. The model reaction was conducted under the optimized conditions. After completion of the reaction, the catalyst was extracted

Fig. 1 TEM image of water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C_{60}-TEGs/PdCl$_2$].

Table 1 Loading rate of PdCl$_2$ on C_{60}-TEGs

$m_{C60\text{-}TEGs}$: m_{PdCl_2} (mg)	Loading rate (%)
10 : 20	83.2
10 : 10	87.3
15 : 10	87.3

Table 2 Optimization of reaction conditions at room temperature[a]

Entry	Catalyst (mol%)	Base	Time (h)	Yield[b] (%)
1	0.1	K_2CO_3	2	98
2	0.05	K_2CO_3	2	98
3	0.025	K_2CO_3	2	96
4	0.01	K_2CO_3	2	95
5	0.005	K_2CO_3	2	86
6	0.01	K_2CO_3	1	91
7	0.01	K_2CO_3	3	96
8	0.01	K_2CO_3	4	98
9	0.01	K_2CO_3	6	98
10	0.01	Na_2CO_3	4	93
11	0.01	$NaHCO_3$	4	90
12	0.01	KF	4	89
13	0.01	K_3PO_4	4	96
14[c]	0.01	K_2CO_3	4	18
15[d]	0.01	K_2CO_3	4	56

[a] Reaction conditions: 1.0 mmol of 4-bromoacetophenones, 1.2 mmol of phenylboronic acid, 2.0 mmol of base, [C_{60}-TEGs/PdCl$_2$] nanocatalyst, 4 mL H_2O. [b] Isolated yields. [c] Reaction conditions: 1.0 mmol of 4-bromoacetophenones, 1.2 mmol of phenylboronic acid, 2.0 mmol of base, PdCl$_2$, 4 mL H_2O. [d] Reaction conditions: 1.0 mmol of 4-bromoacetophenones, 1.2 mmol of phenylboronic acid, 2.0 mmol of base, physical mixture of PdCl$_2$ and C_{60}-TEGS, 4 mL H_2O.

two times with ether (10 mL). The organic phase was concentrated under reduced pressure, and the aqueous phase was recycled directly for the next run. After verification, it could be found that the [C_{60}-TEGs/PdCl$_2$] catalyst could be readily recovered and reused up to five consecutive runs without significant loss in its catalytic activity; the isolated yield was 92% (Fig. 3). The [C_{60}-TEGs/PdCl$_2$] catalyst was also quantitatively analysed by ICP-AES. The analysis showed that after five recycling runs of the catalyst, only 10 wt% of Pd was leached.

Substrate expansion experiment

Encouraged by the results obtained from the coupling reaction of 4-bromoacetophenone with phenylboronic acid in the presence of [C_{60}-TEGs/PdCl$_2$], the scope and generality of the protocol were then expanded to various aryl halides including a range of more challenging aryl chlorides (Table 3). We tested the scope of nanocatalyst [C_{60}-TEGs/PdCl$_2$] in the Suzuki–Miyaura cross-coupling reaction using different *para*-, *meta*- and *ortho*-substituted aryl halides at low catalyst concentrations with optimal reaction conditions, as demonstrated above. When phenylboronic acid was coupled with aryl bromides containing both electron-donating and electro-withdrawing groups, the corresponding products were obtained in excellent yields (entries 1–9, Table 3). Due to the retarding effect in both the oxidative addition and transmetalation processes, the aryl halides or aryl boronic species with *ortho*-methyl substituents exhibited low activities. However, high yields could be achieved with prolonged reaction times (entries 7, 9 and 17, Table 3). From the results, it can be seen that some heteroaryl species were also efficiently
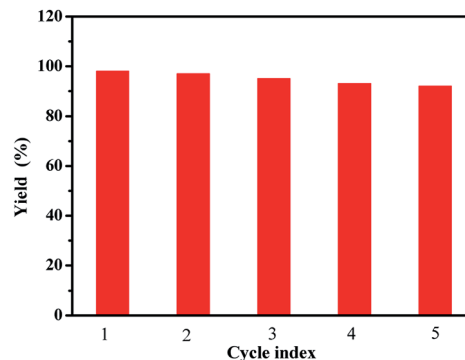

Fig. 3 Recycling of [C_{60}-TEGs/PdCl$_2$] catalyst for the Suzuki–Miyaura coupling reaction under similar conditions.

coupled to provide the corresponding biaryl products in excellent isolated yields (entries 10 and 11, Table 3). The effect of various *para*-substituents on arylboronic acids toward the cross-coupling was examined (entries 12–17, Table 3). No significant difference was observed in the yields or the reaction times. 4-Chloroacetophenone was coupled with 0.5 mol% [C_{60}-TEGs/PdCl$_2$] to obtain 65% yield after 8 h (entry 18, Table 3). When the more challenging 4-chlorotoluene was used, a lower yield was obtained (entry 19, Table 3).

Experimental

Materials and methods

C_{60} fullerene, tetraethylene glycol (TEG), palladium chloride, phenylboronic acid, aryl halides and lithium hydroxide were purchased from Energy chemicals and were used without further purification. Other commercially available reagents were purchased from commercial resources and used without further purification.
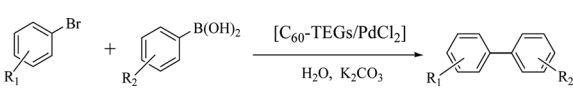
The Pd content of the [C_{60}-TEGs/PdCl$_2$] catalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPE-9000). The size of the nanoparticles of [C_{60}-TEGs/PdCl$_2$] was measured with dynamic laser scattering (DLS, Malvern, Nano ZS90). The morphological examination of [C_{60}-TEGs/PdCl$_2$] was performed by transmission electron microscopy (TEM, JEOL-2100F). The different components of Pd 3d photoelectron peaks of nanocatalyst [C_{60}-TEGs/PdCl$_2$] were determined by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra). Proton nuclear magnetic resonance (NMR) spectroscopy was performed using a Varian 400 MHz spectrometer at room temperature with $CDCl_3$ as a solvent. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra were given in parts per million from the peak for internal tetramethylsilane.
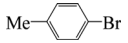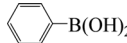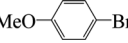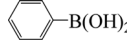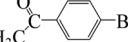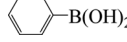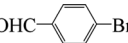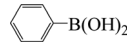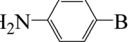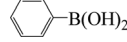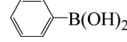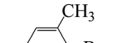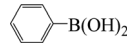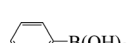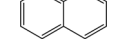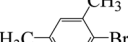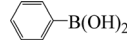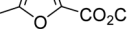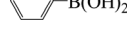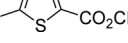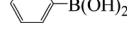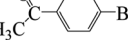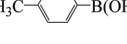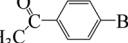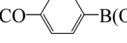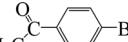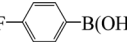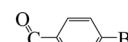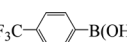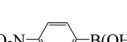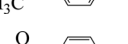
Preparation of water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C_{60}-TEGs/PdCl$_2$]

Water-soluble fullerene nanoparticles of C_{60}-TEGs were synthesized according to previously reported methods.[38–40] The water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C_{60}-TEGs/PdCl$_2$] was prepared by coordination of C_{60}-TEGs with palladium chloride (Scheme 1). Briefly, C_{60}-TEGs were dissolved

Table 3 Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acid catalyzed by [C$_{60}$-TEGs/PdCl$_2$] catalyst under aerobic conditions[a]

Entry	Aryl halide	Aryl boronic	Time (h)	Yield (%)[b]
1	Me—C$_6$H$_4$—Br	—B(OH)$_2$	4	96
2	MeO—C$_6$H$_4$—Br	—B(OH)$_2$	4	95
3	H$_3$C-C(O)—C$_6$H$_4$—Br	—B(OH)$_2$	4	98
4	OHC—C$_6$H$_4$—Br	—B(OH)$_2$	4	97
5	H$_2$N—C$_6$H$_4$—Br	—B(OH)$_2$	4	95
6	Cl—C$_6$H$_4$—Br	—B(OH)$_2$	4	98
7	2-CH$_3$-C$_6$H$_4$-Br	—B(OH)$_2$	6	87
8	1-naphthyl-Br	—B(OH)$_2$	6	91
9	2,4,6-trimethyl-C$_6$H$_2$-Br	—B(OH)$_2$	6	76
10	Br-furan-CO$_2$CH$_3$	—B(OH)$_2$	6	90
11	Br-thiophene-CO$_2$CH$_3$	—B(OH)$_2$	6	92
12	H$_3$C-C(O)—C$_6$H$_4$—Br	H$_3$C—C$_6$H$_4$—B(OH)$_2$	4	97
13	H$_3$C-C(O)—C$_6$H$_4$—Br	H$_3$CO—C$_6$H$_4$—B(OH)$_2$	4	99
14	H$_3$C-C(O)—C$_6$H$_4$—Br	F—C$_6$H$_4$—B(OH)$_2$	4	96
15	H$_3$C-C(O)—C$_6$H$_4$—Br	F$_3$C—C$_6$H$_4$—B(OH)$_2$	4	98
16	H$_3$C-C(O)—C$_6$H$_4$—Br	O$_2$N—C$_6$H$_4$—B(OH)$_2$	4	97
17	H$_3$C-C(O)—C$_6$H$_4$—Br	2-CH$_3$-C$_6$H$_4$-B(OH)$_2$	6	84
18[c]	H$_3$C-C(O)—C$_6$H$_4$—Cl	—B(OH)$_2$	8	65
19[c]	H$_3$C—C$_6$H$_4$—Cl	—B(OH)$_2$	8	30

[a] Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K$_2$CO$_3$ (2.0 mmol), 0.01 mol% [C$_{60}$-TEGs/PdCl$_2$], H$_2$O (4 mL), room temperature. [b] Isolated yields. [c] Reaction conditions: aryl chloride (1.0 mmol), phenylboronic acid (1.2 mmol), K$_2$CO$_3$ (2.0 mmol), 0.5 mol% [C$_{60}$-TEGs/PdCl$_2$], 4 mL EtOH/H$_2$O (V/V, 1 : 1), 80 °C.
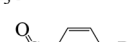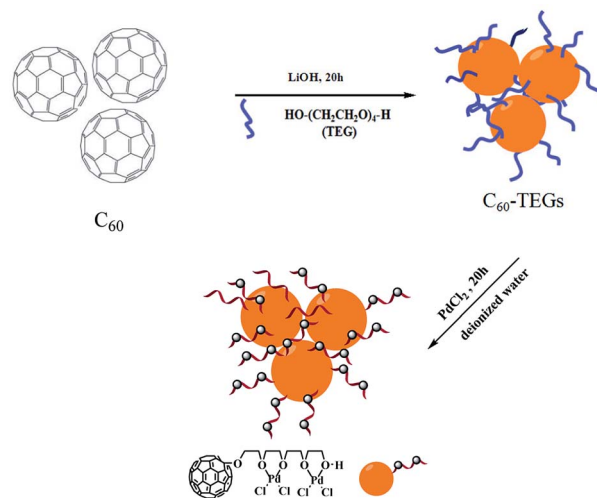

Scheme 1 The synthesis of water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C$_{60}$-TEGs/PdCl$_2$].

in 10 mL deionized water; PdCl$_2$ was added, and the mixture was stirred for 20 h. The precipitate was removed by centrifugation. Next, the solution was purified by dialysis against deionized water using dialysis tubing with a molecular weight cut-off of 3.5 kDa for 48 h to remove unbonded PdCl$_2$ and then lyophilized to obtain [C$_{60}$-TEGs/PdCl$_2$] powders. The powders were dissolved again in deionized water before being used.

Suzuki–Miyaura cross-coupling reaction catalyzed by [C$_{60}$-TEGs/PdCl$_2$]

A 25 mL flask was charged with aryl halide (1.0 mmol), aryl boronic acid (1.2 mmol), K$_2$CO$_3$ (2.0 mmol), catalyst (0.01 mol% Pd), and deionized water (4 mL). The reaction mixture was stirred at room temperature under air for a certain time. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, it was extracted with ether (10 mL). The organic phase was concentrated under reduced pressure and chromatography over silica gel using petroleum ether/ethyl acetate (V/V, 10 : 1) to get the desired coupling products. All the purified products were known compounds and were characterized by comparing their ^{1}H and ^{13}C NMR spectra with those found in literature.[41]

Conclusions

In conclusion, the novel water-soluble fullerene-supported PdCl$_2$ nanocatalyst [C$_{60}$-TEGs/PdCl$_2$] was synthesized. The catalytic system of [C$_{60}$-TEGs/PdCl$_2$] provided a facile and aerial condition for the Suzuki–Miyaura cross coupling reaction of aryl bromides with aryl boronic acids in deionized water with excellent yields of desired products. It is important that [C$_{60}$-TEGs/PdCl$_2$] could be readily recovered and reused up to five consecutive runs by simple extraction without significant loss in its catalytic activity. In addition, the catalytic system of [C$_{60}$-TEGs/PdCl$_2$] showed great tolerance for a broad range of functional groups on the aryl bromides or chlorides. The high catalytic activity, broad substrate scope,

reusability and environmental protection of [C$_{60}$-TEGs/PdCl$_2$] make it a desirable compound from the environmental and industrial viewpoints.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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