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Silyl alkynylphosphine-boranes: key precursors of triazolylphosphines *via* tandem desilylation-Click chemistry†

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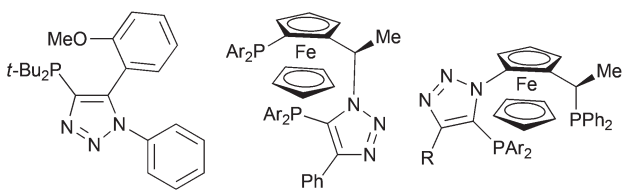
A versatile synthesis of 1,2,3-triazolyl-4-phosphines from the borane complexes of phosphino-alkynes is reported. The efficiency of the procedure relies on the use of readily available silyl-protected alkynyl-phosphine-boranes, which were subjected to desilylation with TBAF followed by copper-catalyzed azide–alkyne-cycloaddition in one pot. Subsequent treatment with DABCO afforded the targeted triazolylphosphines in high yields. The reported method was applied to the synthesis of the first example of an enantioenriched P-stereogenic triazolylphosphine (98.8% ee).

Introduction

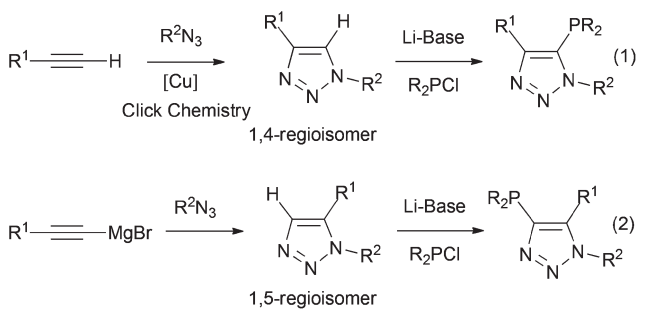
1,2,3-Triazolylphosphines are a new family of ligands recently disclosed in the literature. The electron rich ClickPhos ligand for example (Fig. 1) was shown to display high catalytic activity in the Suzuki–Miyaura cross-coupling and aryl amination reactions involving the poorly reactive aryl chlorides and heteroaryl chlorides.[1] The chiral ferrocenyl ClickFerrophos I ligand (Fig. 1) was able to induce excellent enantioselectivities in asymmetric rhodium- and ruthenium-catalyzed hydrogenation of alkenes and ketones respectively as well as in copper-catalyzed synthesis of pyrrolidines.[2] More recently ClickFerrophos II ligands (Fig. 1) were developed and applied to the enantioselective rhodium-catalyzed hydrogenation of α,β-unsaturated phosphonates.[3]



ClickPhos ClickFerrophos I ClickFerrophos II

Fig. 1 Examples of triazolylphosphine ligands.

Attractive features of triazolylphosphines are the diversity of metal coordination types involving the P-atom and/or N-atom from the triazolyl core,[4] and the potential availability of supported phosphine ligands from polymer-immobilized azides.[5] The major interest in triazolylphosphine ligands stems also from their short and simple preparation based on the Huisgen 1,3-dipolar cycloaddition[6] between azides and alkynes. The triazolyl core is built either through the copper(I)-catalyzed azide/alkyne [3 + 2]-cycloaddition reaction starting from a terminal alkyne (Click reaction)[7,8] or through the [3 + 2]-cycloaddition reaction between azides and alkynyl Grignard reagents[9] leading regioselectively either to 1,4- or 1,5-substituted triazoles respectively (Scheme 1, eqn (1) and (2) respectively). It is noteworthy that eqn (1) and (2) are the key steps of the synthesis of ClickFerrophos and ClickPhos respectively.



Scheme 1 Main reported strategies towards triazolylphosphines.

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The phosphorus moiety is subsequently introduced through deprotonation of the triazole ring by a lithiated base followed by nucleophilic substitution at the phosphorus atom of a chlorophosphine. It is noteworthy that the hydrolysis of the intermediate triazolyl Grignard reagent in pathway 2 can be skipped and the reaction with chlorophosphines can be performed *in situ*.[10] No example of P-stereogenic triazolylphosphines has been reported so far, probably as a result of the limited access and low configurational stability of chiral chlorophosphines.

The alternative pathway based on the use of phosphino-substituted-alkynyl derivatives as Click substrates has only been little explored despite the research interest notably in the asymmetric series in view of the high configurational stability of tertiary phosphines.[11] Evidently phosphines are not suitable substrates because they are converted into iminophosphoranes[12] in the presence of azides through the famous Staudinger reaction.[13] Consequently the few reported triazole syntheses mainly involve oxidized alkynylphosphorus derivatives leading to oxidized derivatives, which have to be first reduced to deliver the expected ligand.[4,14,15] A valuable alternative would be to use protected phosphines such as phosphine-borane complexes, which are known to undergo decomplexation under mild conditions.[16] Only one example could be found in the literature,[17] probably because terminal alkynylphosphine-boranes are sensitive molecules. They may react as Michael acceptors undergoing nucleophilic addition to the triple bond. Side reactions resulting from the deprotonation of the terminal carbon atom may also occur. We reasoned that these side reactions could be circumvented and the stability of the starting alkynylphosphine-boranes could be enhanced by introducing a silyl group at the terminal carbon atom. According to our planned retrosynthetic sequence, the targeted triazolylphosphines **1** would result from the decomplexation of their borane complexes **2**, which would be available from the click reaction between azides and terminal alkynes **3**, *in situ* generated through the desilylation of alkynylphosphine-boranes **4** (Scheme 2).

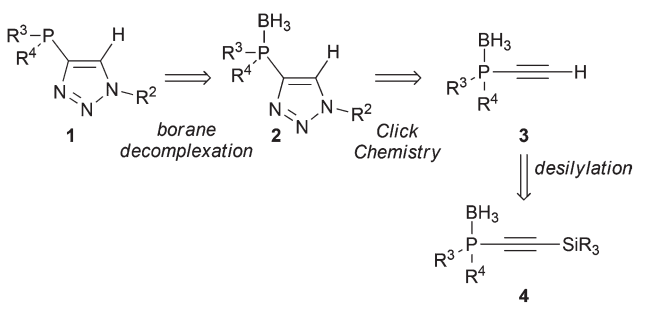
Our strategy could give access to a broad range of achiral and chiral P-stereogenic triazolylphosphines **1** notably by taking advantage of our recently reported synthesis of alkynylphosphine-boranes, based on the copper-catalyzed cross-coupling reaction between secondary diaryl-, dialkyl- or alkylarylphosphine-boranes and 1-bromoalkynes.[18,19]

Results and discussion

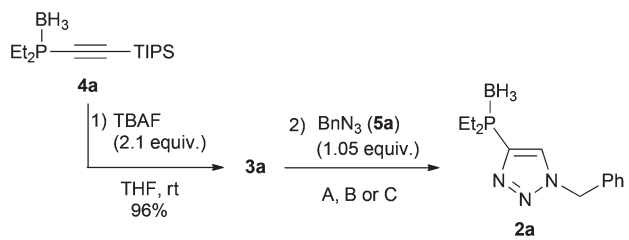
We first examined the transformation of alkynylphosphine-boranes **4** into 1,4-substituted 1,2,3-triazoles **2** step by step using (triisopropylsilyl)ethynyl-diethylphosphine-borane (**4a**)[18] as a model substrate. The desilylation of **4a** was readily achieved at room temperature using TBAF[20] as a desilylating reagent (2.1 equiv.) in THF (Scheme 3). The resulting terminal alkyne **3a** (δ_P = 11.9 ppm) was isolated in 96% yield after silica gel chromatography. It was then subjected to the classical Click reaction conditions with benzyl azide (**5a**).[7a,21] A copper(II) complex, copper sulfate pentahydrate (10 mol%), was used in the presence of sodium ascorbate (20 mol%) to reduce the metal complex into a copper(I) complex, which is the active species in this reaction. This catalytic system, which is aimed to limit the oxidation of the copper(I) complex, requires a biphasic solvent system *tert*-butanol–water (1 : 1) to solubilize sodium ascorbate. Under these reaction conditions, alkyne **3a** was converted into the expected triazole **2a** (δ_P = 7.6 ppm) in a reasonable 65% isolated yield after overnight stirring at room temperature.

Terminal alkyne **3a** being a Michael acceptor, we were concerned by its stability in the chosen aqueous solvent system. Consequently anhydrous conditions were also tested to perform the [3 + 2]-cycloaddition between **3a** and azide **5a**. They consisted of using copper(I) thiophenecarboxylate (CuTC) as a catalyst in toluene.[22] After 3 hours at room temperature, a full conversion of **3a** into triazole **2a** was observed, but the isolated yield of **2a** was not improved (65%). We also tested our previously reported well-defined copper(I) complex [phenCuIPHPh$_2$][23] because it is structurally related to [CuBr(PPh$_3$)$_3$], a complex which was successfully used as a Click catalyst.[24] In this case, the full conversion was reached after 10 h and triazole **2a** was satisfactorily obtained in a higher yield of 77%.

In order to improve the procedure efficiency by skipping the isolation of sensitive terminal alkynylphosphine-boranes **3**, we evaluated the feasibility of the one-pot transformation of alkynylphosphine-boranes **4** into 1,4-substituted 1,2,3-triazoles



Scheme 2 Envisioned retrosynthetic sequence towards 1,2,3-triazolyl-4-phosphines.



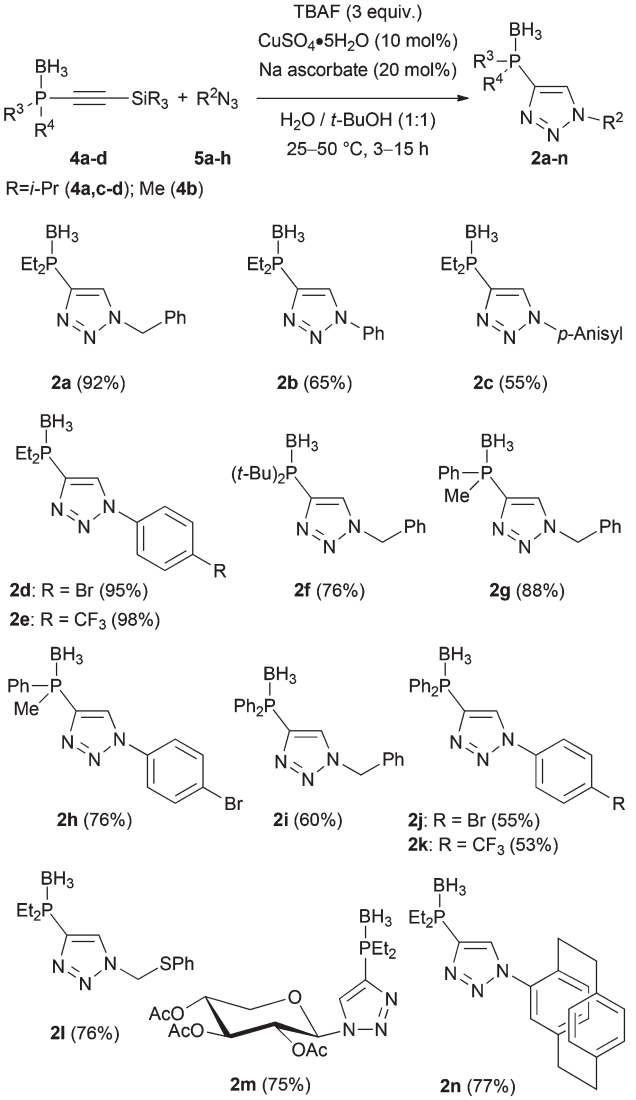
Scheme 3 Stepwise synthesis of triazolylphosphine **2a** from **4a**.

2 through tandem desilylation and Click chemistry. The reaction between silylated alkynylphosphine borane **4a** and azide **5a** was chosen as a model reaction for this study. When two equivalents of TBAF were added to the classical Click reaction conditions (*vide supra*), the formation of triazole **2a** was not observed, but only a partial desilylation of **4a** was observed leading to **3a**. This observation probably results from the high solvation of the fluoride ion in water, which makes it less nucleophilic[25] and slows down the desilylation process. In order to counterbalance this effect the amount of TBAF was increased to three equivalents. After 3 h at 25–30 °C, a full conversion of **4a** was observed and the targeted triazole **2a** was isolated in 92% yield after silica gel chromatography, demonstrating the superiority of the tandem reaction over the two-step procedure. Importantly, the isolated yield of triazole **2a** was up-graded to 99% when the reaction was scaled up to 2 g of the starting alkynylphosphine-borane **4a**.

The scope of the one-pot desilylation/[3 + 2]-cycloaddition reaction procedure was then investigated by varying the azide substitution pattern and the phosphine reagents. The results are displayed in Scheme 4. The reaction of **4a** with phenylazide (**5b**) and 4-anisylazide (**5c**) was not efficient at room temperature. The expected triazoles **2b** and **2c** were finally obtained in 65 and 55% respective yields provided that the reaction was run at 50 °C. On the other hand, the reaction of **4a** with the electron deficient aryl azides **5d** and **5e** bearing a bromide or a trifluoromethyl group in the *para*-position, respectively, readily proceeded at 25–30 °C, and afforded the corresponding triazoles **2d** and **2e** in 95 and 98% yield respectively. The structures of triazoles **2c** and **2d** were confirmed by X-ray diffraction analysis (see ESI†). In agreement with the well-established regioselectivity of the copper-catalyzed version of the Huisgen 1,3-dipolar cycloaddition, the phosphorus moiety is located at position 4.

The scope of phosphine reagents was also evaluated. The reaction of benzyl azide (**5a**) with TMS-ethynyl-di-*tert*-butylphosphine-borane (**4b**) (R^3 = R^4 = *t*-Bu, R = Me) afforded the corresponding triazole **2f** in 76% yield after 3 h at 30 °C. The reaction conditions were also successfully applied to the synthesis of P-stereogenic triazolylphosphines **2g** and **2h** through the reaction of methyl-phenyl-alkynylphosphine-borane **4c** with **5a** and aryl azide **5d** respectively. Triazolylphosphines **2g** and **2h** were isolated in 88% and 76% yields respectively. Diphenyl-alkynylphosphine **4d** also underwent the tandem desilylation/[3 + 2]-cycloaddition reaction with various azides. The corresponding diphenyltriazolylphosphine-boranes **2i–k** were isolated in yields between 53 and 60%. These lower yields can be ascribed to the weakness of the phosphorus–boron bond when the phosphorus substituents are weak electron donors like phenyl groups.

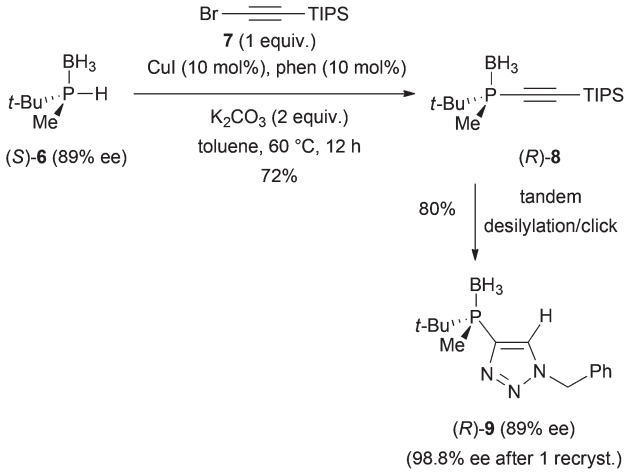
To further illustrate the potential of our procedure the reaction of **4a** with more complex structures of azides was briefly surveyed. Thus functionalized azides **5f** and **5g** bearing a sulfanyl and a sugar function respectively were tested and shown to readily undergo the transformation under the defined reaction conditions. The corresponding triazoles **2l** and **2m** were



Scheme 4 Scope of the tandem desilylation/Click reaction between alkynylphosphine-boranes and azides.

obtained in 76 and 75% yields respectively. The reaction of **4a** with azido[2.2]paracyclophane (**5h**) was also attempted as an entry to [2.2]paracyclophane-derived triazolyl monophosphine ligands, which have recently appeared in the literature.[26] The reaction was optimally performed at 40 °C for 15 h and delivered the targeted triazole **2n** in 77% yield. The structure of **2n** was confirmed by X-ray diffraction analysis (see ESI†). It is worth pointing out that the access to triazoles **2d**, **2h**, **2j** or **2m** would be difficult through pathways involving a lithium base (Scheme 1, eqn (1) and (2)) because of the presence of sensitive bromide or acyl functional groups.

Borane deprotection of alkyl-aryl- and diaryl-triazolylphosphine-boranes **2g** and **2i–k** was readily achieved by treatment with DABCO[27] (2 equiv.) in THF at 60 °C. The corresponding triazolylphosphines **1g** and **1i–k** were isolated in 71%, 92%, 91% and 97% respective yields. With electron rich phosphine derivatives, such as diethyl-triazolylphosphine-boranes **2a**, **2c**



Scheme 5 Application to the synthesis of enantioenriched P-stereogenic triazolylphosphine-borane (*R*)-**9**.

and **2e**, the decomplexation was optimally performed with a higher amount of DABCO (3 equiv.) in THF at 70 °C and delivered the triazoles **1a**, **1c** and **1e** in 74%, 61% and 88% respective yields. The structures of triazoles **1e**, **1i** and **1j** were confirmed by X-ray diffraction analysis (see ESI†).

The synthesis of an enantioenriched P-stereogenic triazolylphosphine was the next goal of this work. To the best of our knowledge none of the chiral triazolylphosphines reported so far are P-stereogenic.[2,3,26] Chiral P-stereogenic phosphines,[11a,28] by bringing chirality closer to the metal, are quite interesting ligands for asymmetric catalysis. For this study enantioenriched (*S*)-*tert*-butylmethylphosphine-borane (**6**) (89% ee)[29] was submitted to Cu(I)-catalyzed cross-coupling with 1-bromo-2-TIPS-acetylene (**7**) according to our previously described method (Scheme 5).[18] The resulting alkynylphosphine-borane **8** was isolated in 72% yield, and then readily converted into triazolylphosphine-borane **9** in 80% yield *via* the tandem desilylation/Click procedure.

The enantiomeric excess of **9** was determined as 89% ee according to chiral HPLC analysis demonstrating the retention of stereopurity along the reaction sequence. Interestingly the enantiomeric excess could be increased to 98.8% after a single recrystallization from dichloromethane/pentane. Moreover single crystals of **9** suitable for X-ray diffraction analysis could be obtained allowing us to assign the (*R*)-configuration to **9** according to its X-ray-structure (Fig. 2). Consequently the (*R*)-configuration can be also assigned to alkynylphosphine-borane **8** demonstrating that the copper(I)-catalyzed cross-coupling reaction between secondary phosphine-boranes and 1-bromoalkynes proceeds with retention of the configuration at phosphorus.

We next performed preliminary studies on the catalytic activity of the newly synthesized triazolylphosphines with compound **2f**, which has a structure close to that of the ClickPhos ligand (Scheme 4 and Fig. 1). Borane decomplexation of **2f** by treatment with DABCO (5 equiv.) afforded triazolylphosphine **1f**, which was directly converted into the palladium(II) complex

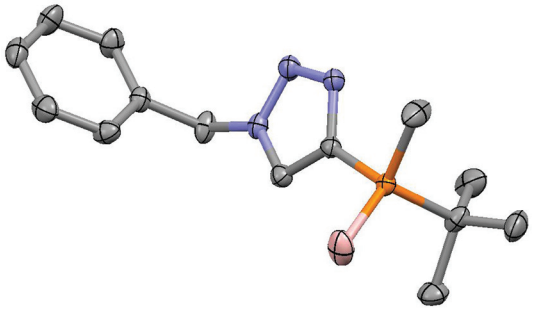
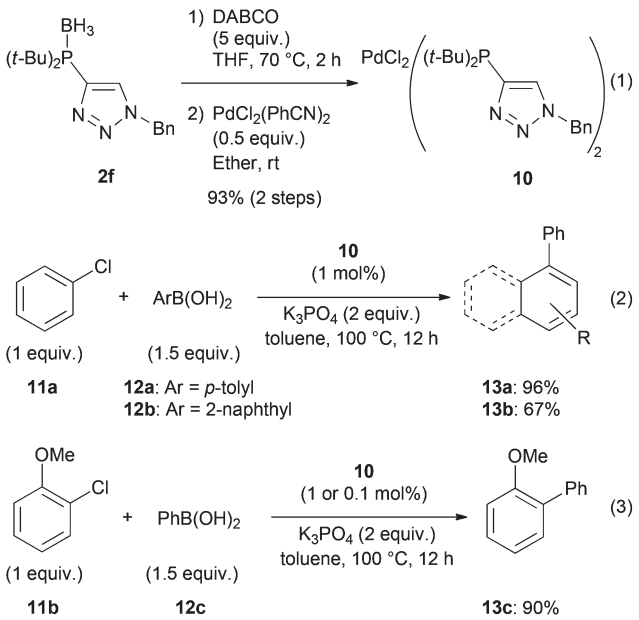


Fig. 2 X-ray structure of triazolylphosphine-borane (*R*)-**9**.



Scheme 6 Synthesis of palladium(II) complex **10** (eqn (1)) and application to the Suzuki–Miyaura cross-coupling of chlorobenzene (**11a**) with arylboronic acids **12a–b** (eqn (2)) and of *ortho*-anisyl chloride (**11b**) with phenylboronic acid (**12c**) (eqn (3)).

10 in 93% isolated yield through reaction with $[PdCl_2(PhCN)_2]$ (Scheme 6, eqn (1)). The expected square planar *trans*-$[PdCl_2(\mathbf{1f})_2]$ structure of **10** for steric reasons was confirmed by X-ray diffraction analysis (Fig. 3).

Gratifyingly, complex **10** (1 mol%) was shown to catalyze the Suzuki–Miyaura cross-coupling of poorly reactive chlorobenzene (**11a**) with *p*-tolyl boronic acid (**12a**) affording the expected bis-arene **13a** in 96% isolated yield (Scheme 6, eqn (2)). The Suzuki cross-coupling of **11a** with the more sterically hindered naphthyl boronic acid (**12b**) afforded the corresponding bis-aryl product **13b** in 67% isolated yield (Scheme 6, eqn (2)). Complex **10** (1 mol%) also efficiently catalyzed the cross-coupling between *ortho*-anisyl chloride (**11b**) and phenylboronic acid (**12c**) delivering the corresponding adduct **13c** in 90% isolated yield (Scheme 6, eqn (3)). Importantly the yield of bis-arene **13c** was not affected when the catalyst loading was

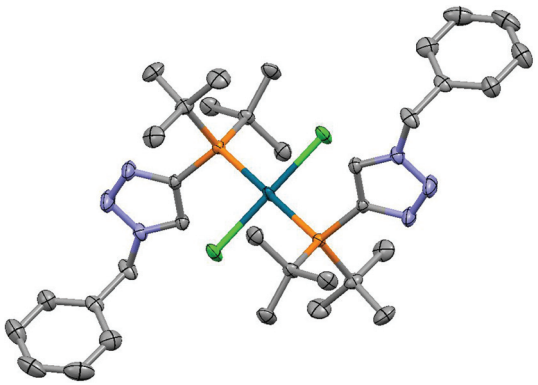


Fig. 3 X-ray structure of palladium(II) complex **10**.

reduced to 0.1 mol%. These first results demonstrate that complex **10** derived from triazolylphosphine **2f** is a highly active catalyst in the Suzuki–Miyaura cross-coupling reactions of aryl chlorides.

Conclusion

We developed an efficient synthesis of 1,2,3-triazolyl-4-phosphines from silyl alkynylphosphine-boranes, relying on a tandem desilylation with TBAF/Click transformation and subsequent decomplexation by treatment with DABCO. The procedure is general, being readily applicable to diaryl-, dialkyl- and alkyl-aryl-P derivatives and to benzyl- and aryl-azides. The presence of sensitive functional groups such as a halide or an acetyl group is tolerated in contrast to previously reported triazolylphosphine syntheses, which involved the use of metallic bases. Various original functional groups such as a sugar, a sulfanyl moiety or a paracyclophane could also be introduced. Moreover the first example of an enantioenriched P-stereogenic 1,2,3-triazolyl-4-phosphine was available in high yields through the reported methodology. Our preliminary studies on the use of a palladium complex derived from triazolylphosphine **2f** in the Suzuki cross-coupling reactions with unactivated aryl chlorides are quite promising. The synthesis and use in catalysis of further metallic complexes derived from the synthesized triazolylphosphines and notably from the chiral ones is the goal of our future studies.

Acknowledgements

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