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Research paper Catalytic hydrosilylation of olefins and ketones by base metal complexes bearing a 2,2':6',2"-terpyridine ancillary ligand



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ARTICLE INFO	A B S T R A C T
Keywords: Hydrosilylation Catalytic reaction Terpyridine ligand Olefines and ketones	The activities of $[M(tpy)Br_2]$ (M = Mn, Co, Ni, or Cu) for the hydrosilylation of olefins and ketones were investigated in the presence of NaBHEt ₃ as an activator. $[Co(tpy)Br_2]$ and $[Ni(tpy)Br_2]$ showed catalytic activities for the hydrosilylation of 1-octene with diphenylsilane. In particular, $[Co(tpy)Br_2]$ showed good catalytic ac- tivity. The linear anti-Markovnikov hydrosilylation product was predominant; however, a small quantity of the branched Markovnikov product was also produced. Generation of the branched product was suppressed by the addition of THF and pyridine as solvents. The reactivities of other olefins and silanes were also examined. In the hydrosilylation of ketones, unlike the hydrosilylation of 1-octene, all four complexes used in this study exhibited catalytic activity. Interestingly, in the reaction between diphenylsilane and acetophenone, the dominant product was the 1:2 double hydrosilylation product, not the 1:1 single hydrosilylation product, even in a reaction mixture of equal parts diphenylsilane and acetophenone.

1. Introduction

Hydrosilylation of unsaturated organic compounds catalyzed by transition metal complexes is among the best methods to obtain organosilane compounds due to their simplicity and atom economy. In this field, the creation and development of base metal catalysts as alternatives to conventional Pt catalysts is a popular topic. A number of base metal catalysts exhibit catalytic activity for hydrosilylation, and many of them have a pincer-type ligand, such as NNN [1-4] and PNN types [1,5]. These ligands usually contain bulky substituents that promote stereoand/or regioselective hydrosilylation products. Our group reported Fe and Co complexes bearing an iminobipyridine ligand. The Fe complexes show good catalytic activity for both olefins and ketones [3,4], while the Co complexes have good chemoselectivity for olefin hydrosilylation, which can easily be switched to ketone selectivity by the addition of pyridine to the reaction system [4b]. These sophisticated stereo- and chemo-selectivities are due to the well-organized ligands. If base metal complexes with ubiquitous pincer ligands, not specially customized ligands, show good catalytic activities, these complexes could have useful applications.

2,2':6',2"-Terpyridine (tpy) is one of the simplest pincer ligands and is thermally and chemically stable, inexpensive, and commercially available. Therefore, it is important to evaluate and compare the catalytic activity for hydrosilylation of base metal complexes with tpy as a ligand. Some base metal complexes bearing a tpy ligand have been prepared, but their catalytic activities for hydrosilylation have not been reported. The catalytic activity has been reported only for [Co(tpy)Cl₂] [1b] and [Co(tpy)(OAc)(THF)₂](OAc) [2h]. However, since these complexes have different chemical formulas and their catalytic activities were measured under different reaction conditions, their catalytic activities cannot be directly compared.

In this study, we synthesized base metal complexes with the same chemical formula containing one tpy ligand, and then examined and compared their catalytic activities under the same hydrosilylation conditions. The first-row transition metals from groups 7 to 11, viz. Mn, Fe, Co, Ni, and Cu, were selected, and the syntheses of their $[M(tpy)Br_2]$ complexes were attempted. The complexes for Mn, Co, Ni, and Cu were successfully prepared. In contrast, $[Fe(tpy)Br_2]$ could not be obtained. This is consistent with the following findings [6]; $[Fe(tpy)X_2]$ (X = Cl, Br) with unsubstituted tpy cannot be isolated because it becomes [Fe (tpy)_2][FeX_4] due to disproportionation, whereas $[Fe(tpy)X_2]$ with substituted tpy at the 6 and/or 6" position can be isolated because the disproportionation is disturbed by steric repulsion between the substituted tpy's.

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2. Experimental section

2.1. General information

All the reactions were carried out under N₂ using Schlenk techniques. ¹H NMR spectra were recorded using a JEOL JNM-AL 400 spectrometer. The residual peaks of the solvent or TMS were used as internal standards. GC analyses were carried out using a Shimadzu GC-2014 equipped with an Rtx-5MS (RESTEC, 30 m, 0.25 mm ID, 0.25 μ m) capillary column. Product yields were determined based on the calibration curve of each authentic sample. FAB-MS measurements were recorded using a JEOL JMS-700(2).

2.2. Materials

 $[Cu(tpy)Br_2]$ was synthesized according to a reported procedure [7]. $[M(tpy)Br_2]$ (M = Mn, Co, and Ni) were prepared by reported procedures with a slight modification, as shown below. All other reagents were purchased from commercial sources and used as received.

2.2.1. Preparation of [Mn(tpy)Br₂]

[Mn(tpy)Br₂] was synthesized by a procedure similar to that of [Mn (tpy)Cl₂] reported previously [8]. MnBr₂ (107 mg, 0.50 mmol) was dissolved in EtOH (2.0 mL), and a solution of 2,2':6',2"-terpyridine (117 mg, 0.50 mmol) in EtOH (2.0 mL) was added. During stirring, a pale yellow precipitate formed. After 15 min of stirring, the resulting precipitate was collected by filtration, washed with EtOH (10 mL) and ether (10 mL), and dried in vacuo. Yield: 207 mg (92%). Anal. Calcd for $C_{15}H_{11}Br_2N_3Mn$: C, 40.26; H, 2.67; N, 9.19. Found: C, 40.21; H, 2.47; N, 9.38. HRMS (FAB): [M-Br]⁺ Calcd. for $C_{15}H_{11}BrN_3Mn$: 366.9517. Found: 366.9498.

2.2.2. Preparation of [Co(tpy)Br₂]

This compound was prepared by the published procedures for [Co (tpy)Cl₂] [9] with a slight modification. CoBr₂ (87.5 mg, 0.40 mmol) and tpy (93.3 mg, 0.40 mmol) were dissolved in THF (15 mL). During stirring, a brown precipitate was formed. MeOH (3.0 mL) was added, resulting in a color change from brown to emerald green. After stirring for 24 h, the precipitate was collected by filtration. The emerald green powder obtained was washed with small portions of MeOH and ether, and then dried in vacuo. Yield: 170 mg (94%). Anal. Calcd for C₁₅H₁₁Br₂N₃Co·0.5H₂O (M + 0.5H₂O): C, 39.08; H, 2.62; N, 9.11. Found: C, 39.34; H, 2.53; N, 9.14. HRMS(FAB): [M-Br]⁺ Calcd. for C₁₅H₁₁BrN₃Co: 370.9468. Found: 370.9479.

2.3. General procedure of hydrosilylation

[M(tpy)Br₂] (5.4 µmol) was dispersed in a mixture of 1-octene (0.85 mL, 5.4 mmol) and diphenylsilane (1.0 mL, 5.4 mmol) with/without 1.0 mL of a solvent in the Schlenk tube under N₂. Sodium triethylborohydride (NaBHEt₃) (108 µL, 1.0 M in toluene) was then added to the suspension to initiate the reaction. The solution was stirred at a controlled temperature. After 24 h, the reaction was halted by the removal of the catalyst and excess NaBHEt₃ using a flash column (silica). The yields and turnover numbers (TONs) of the products were determined by GC. The yield and TON of hydrosilylation products from styrene and PhMe₂SiH (**81** and **8v**) [11] were determined by NMR using an internal standard (dimethyl sulfone).

2.4. Hydrosilylation of 1-octene with diphenylsilane by changing the concentration of $[Co(tpy)Br_2]$

In Schlenk tubes, 2.4, 12, and 24 mg of $[Co(tpy)Br_2]$ (5.4, 27, and 54 mmol for 0.1, 0.5, and 1.0 mol%, respectively) were dispersed in a mixture of 1-octene (0.85 mL, 5.4 mmol) and diphenylsilane (1.0 mL, 5.4 mmol) under N₂. Sodium triethylborohydride (NaBHEt₃) (1.0 M in toluene, 20 times the amount of $[Co(tpy)Br_2]$) was then added to the suspension to initiate the reaction. After stirring for 24 h, the reaction was halted by the removal of the catalyst and excess NaBHEt₃ using a flash column (silica). The yields and TONs of the products were determined by GC.

3. Results and discussion

3.1. Catalytic activity of [M(tpy)Br₂]

In general, $[M(tpy)Br_2]$ is considered not to be a real catalytic species but a pre-catalyst instead. To produce the active species, $[M(tpy)Br_2]$ is often reduced in advance or in situ [1–5]. In this study, an excess of NaBHEt₃ was used to reduce $[M(tpy)Br_2]$. The hydrosilylation of 1octene with diphenylsilane (Ph₂SiH₂) was employed as a model reaction (Eq. 1) to evaluate the catalytic activity of each complex.

In a 1:1 M mixture of 1-octene and Ph₂SiH₂, [M(tpy)Br₂] (0.1 mol% of the olefin or hydrosilane) was dispersed under N₂. Then, 2.0 mol% of NaBHEt₃ in toluene solution was added to initiate the reaction. After stirring the solution for 24 h at 25 °C, the reaction mixture was analyzed by GC.



(1).

2.2.3. Preparation of [Ni(tpy)Br₂]

This complex was prepared by the procedure similar to that in the previous report [10] with a little modification. To a solution of NiBr₂·3H₂O (117 mg, 0.43 mmol) in THF (25 mL), 2,2':6',2"-terpyridine (100 mg, 0.43 mmol) in THF was added drop-wise over 10 min. The mixture was stirred for 24 h, resulting in the formation of a pale green precipitate. The precipitate was collected by filtration and washed with THF (10 mL) and ether (10 mL). Vacuum drying yielded 194 mg of [Ni (tpy)Br₂] as a pale green powder (84%). Anal. Calcd for C₁₅H₁₁Br₂N₃Ni·1.5H₂O: C, 37.63; H, 2.95; N, 8.87. Found: C, 37.76; H, 3.37; N, 9.33. HRMS(FAB): [M-Br]⁺ Calcd. for C₁₅H₁₁BrN₃Ni: 369.9190. Found: 369.9494.

The results are shown in Table 1. Hydrosilylation of 1-octene with Ph₂SiH₂ (Eq. (1)) produces two possible product types: the linear (anti-Markovnikov) (1l) and branched (Markovnikov) (1b) products. [Co(tpy)

Table 1

Hydrosilylation of 1-octene with Ph_2SiH_2 in the presence of $[M(tpy)Br_2]$ and $NaBHEt_3.$

Entry	Pre-catalyst	Yield of 11 ^{a,b}
1	[Mn(tpy)Br ₂]	No reaction
2	[Co(tpy)Br ₂]	84%
3	[Ni(tpy)Br ₂]	40%
4	[Cu(tpy)Br ₂]	No reaction

^a Determined by GC. ^bBased on 1-octene, namely also Ph₂SiH₂.

 Br_2] and [Ni(tpy) Br_2], activated by NaBHEt₃, served as catalysts to generate the corresponding hydrosilylation compounds, which mainly comprised the linear product (11); 84% and 40% for [Co(tpy) Br_2] and [Ni(tpy) Br_2], respectively. On the other hand, when [Mn(tpy) Br_2] and [Cu(tpy) Br_2] were used as pre-catalysts, no products were detected. Therefore, [Co(tpy) Br_2] demonstrated the best catalytic activity for hydrosilylation among the four base metal complexes; a small amount of the branched product (1b) (4.0%) was also formed.

The catalytic activity of $[M(tpy)Br_2]$ in the absence of NaBHEt₃ and that of NaBHEt₃ itself were also investigated. Both $[Co(tpy)Br_2]$ and $[Ni(tpy)Br_2]$ showing catalytic activity with the help of NaBHEt₃ did not show any catalytic activity in the absence of NaBHEt₃. Addition of 2.0 mol% of NaBHEt₃ to the mixture of 1-octene and Ph₂SiH₂ in the absence of any $[M(tpy)Br_2]$ produced a small amount of **11** (7.0% based on the substrate). These results indicate that the complex derived from $[M(tpy)Br_2]$ and NaBHEt₃ is an actually active species

3.2. Optimization of [Co(tpy)Br₂] catalysis

Since $[Co(tpy)Br_2]$ exhibited good catalytic activity, the temperature dependence of the hydrosilylation with Ph₂SiH₂ using $[Co(tpy)Br_2]$ was examined (Table 2). As the temperature was increased from 25 °C, the yield of the hydrosilylation product (11) gradually decreased. At 100 °C, only 54% yield was recorded. This may be due to decomposition of the active species derived from $[Co(tpy)Br_2]$ at higher temperatures. The regioselectivity for 11 was ranged from 0.94 to 0.98 at each temperature. Since the reaction at 25 °C showed the best result, subsequent reactions were performed at this temperature

Next, the hydrosilylation of 1-octene with Ph_2SiH_2 in the presence of various amount of $[Co(tpy)Br_2]$ was examined at 25 °C (Table 3). When the amount of the pre-catalyst $[Co(tpy)Br_2]$ was changed from 0.1 mol% to 1.0 mol% based on 1-actene, namely also Ph_2SiH_2 (concentration of the complex; ca. 2.9–29 mM), the yield of **11** was approximately constant (84%), but the yield of **1b** increased from 4.0% to 15%. In addition, the total yield increased from 88% to 99%. Therefore, an increase in the amount of catalyst from 0.1 mol% to 1.0 mol% caused an increase in the yield of the branched product but not that of the linear product, which led to an increase in total yield. However, this also led to a decrease in selectivity and a significant decrease (almost one-tenth) in the catalytic TON. In terms of regioselectivity and TON, it can be said that a reaction using 0.1 mol% [Co(tpy)Br_2] (Entry 1) is preferable.

3.3. Solvent effect on [Co(tpy)Br₂] catalysis

Hydrosilylation reagents, such as hydrosilanes and olefins, are usually liquid, implying that no solvent is required for the reaction. However, when solid reactants are used, a solvent is needed. Thus, solvent effects on hydrosilylation catalyzed by $[Co(tpy)Br_2]$ were investigated.

Toluene, THF, hexane, and pyridine were employed as solvents. An equal volume of solvent to that of Ph_2SiH_2 was added, and the same reaction conditions used for Entry 1 in Table 3 were applied. The results of the product examination are shown in Table 4. The results for toluene

Table 2

Temperature dependence on hydrosilylation of 1-octene with Ph_2SiH_2 catalyzed by [Co(tpy)Br₂].

Entry	Temperature	Yield ^{a,b}		Total yield	Selectivity for 11 ^c
		11	1b		
1	25 °C	84%	4.0%	88%	0.95
2	40 °C	84%	5.4%	89%	0.94
3	60 °C	79%	3.0%	82%	0.96
4	80 °C	74%	2.7%	77%	0.96
5	100 °C	54%	1.1%	55%	0.98

^a Determined by GC. ^bBased on 1-octene, namely also Ph_2SiH_2 . ^cSelectivity for 11 = (yield of 11)/(total yield).

Table 3

Concentration dependence of $[Co(tpy)Br_2]$ on hydrosilylation of 1-octene with Ph_2SiH_2 .

Entry	Amount of [Co (tpy)Br ₂] ^b	Yield ^{a,b}		Total	TON	Selectivity for
		11	1b	yield		11 ^c
1	0.1 mol%	84%	4.0%	88%	880	0.95
2	0.5 mol%	85%	12%	97%	194	0.88
3	1.0 mol%	84%	15%	99%	99	0.85

 $^a\,$ Determined by GC. bBased on 1-octene, namely also $Ph_2SiH_2.\ ^cSelectivity$ for 11 = (yield of 11)/(total yield).

Table 4

Solvent effect on hydrosilylation of 1-octene with Ph_2SiH_2 catalyzed by [Co(tpy) Br_2].

Entry	Solvent	Yield ^{a,b}		Total yield	Selectivity for 11^{c}
		11	1b		
1	toluene	85	4.0	89	0.96
2	hexane	82	8.0	90	0.91
3	THF	98	2.0	100	0.98
4	pyridine	90	N.D.	90	>0.99

^a Determined by GC. ^bBased on 1-octene, namely also Ph_2SiH_2 . ^cSelectivity for 11 = (yield of 11)/(total yield).

and hexane (Table 4, Entries 1 and 2) were similar to those in the absence of solvent (Table 3, Entry 1). The results for THF were the best in terms of yield and regioselectivity (Entry 3). We previously reported that a Co complex with an iminobipyridine derivative ligand showed catalytic activity for the hydrosilylation of olefins, and the addition of pyridine to the reaction system suppressed hydrosilylation [4]. In contrast, the results of Entry 4 in Table 4 show that pyridine behaved as a favorable solvent (90% yield of 11 and quite high selectivity (>0.99) of 11).

With THF and pyridine as a solvent, the total yield and the selectivity were improved, respectively. Since both solvents have coordination ability, it is possible that they act as additional ligands during hydrosilylation. For simple reasons that tpy is used as a metal ligand in this study and is a pyridine analog, the effect of adding tpy was examined. Excess tpy (10 eq toward [Co(tpy)Br₂], 1.0 mol% based on 1-octene, namely also Ph₂SiH₂) was added to the reaction system shown in Eq. 1. As a result, the yields of **11** and **1b** were 85% and 3.3%, repsevtively, and the selectivity was 0.96. These results were very similar to those obtained without tpy (Table 2, Entry 1). In other words, the effect observed with pyridine was not observed with the addition of tpy. The details of the effect of pyridine are currently unknown.

3.4. Hydrosilylation of olefins with a functional group

Hydrosilylation of functionalized olefins with Ph₂SiH₂ catalyzed by [Co(tpy)Br₂] was conducted under the same reaction conditions as described for Eq. 1, as shown in Eq. 2. The results are summarized in Table 5. When styrene and vinylcyclohexane were employed as olefin substrates, the corresponding linear hydrosilylation products were generated in excellent yields (Entries 1 and 2). In both cases, the corresponding branched products were not formed; when 1-octene was used, a small amount of the branched product was formed (Table 2). Dimethylallylamine was also converted to the corresponding product (4), but the yield was moderate (53%). When 1,2-epoxy-5-hexene was used (Entry 4), a complicated process took place. The hydrosilylated product was formed, but the yield was very low (7%); the other products could not be identified. Allyl chloride, vinyl acetate, and methyl acrylate (Entries 5-7) were not converted into the corresponding hydrosilylation products, and the olefins remained unchanged according to NMR measurements. These functional groups probably inactivate the catalytically active species.

Table 5



^a Determined by GC. ^bBased on olefin, namely also Ph₂SiH₂.



3.5. Hydrosilylation using various silanes

Since hydrosilylation reactions with a secondary silane have been described above, this section describes the results when primary and tertiary silanes are used. Here, styrene was used as an olefin to simplify the reaction system. When 1-octene was used, linear and branched hydrosilylation products were formed, whereas when styrene was used, only a linear product was formed (Table 5). When phenylsilane (PhSiH₃) was used, only the linear product (6) was produced in good yield (Eq. 3). Triethoxysilane (HSi(OEt)₃) and dimethylphenylsilane (PhMe₂SiH) were selected as tertiary silanes. Triethoxysilane afforded the linear hydrosilylation product (7) with a moderate yield (Eq. 4). For dimethylphenylsilane (Eq. 5), the linear hydrosilylation product (81) was produced in 66% yield. In addition, the vinyl (dehydrogenative silylation) product (8v) was produced in 11% yield. The vinyl product was found only in the reaction using PhMe₂SiH. The reaction mechanism is unclear; however, these results indicate that the [Co(tpy)Br₂] catalyst

Table 6

Hydrosilylation of acetophenone with Ph₂SiH₂ catalyzed by [M(tpy)Br₂].

Entry	Catalyst	Yield (TON) ^{a,b}		Total yield	Selectivity for
		9s	9d	(TON)	9d ^c
1	[Mn(tpy)	30%	29%	59% (880)	0.49
	Br ₂]	(300)	(580)		
2	[Co(tpy)	25%	31%	56% (870)	0.55
	Br ₂]	(250)	(620)		
3	[Ni(tpy)	11%	36%	47% (830)	0.77
	Br ₂]	(110)	(720)		
4	[Cu(tpy)	20%	31%	51% (820)	0.60
	Br ₂]	(200)	(620)		

^a Determined by GC. ^bBased on acetophenone, namely also Ph_2SiH_2 . ^cSelectivity for **9d** = (yield of **9d**)/(total yield).

system may be applied to tertiary silanes, even though tertiary silanes are generally known to have poor participation in hydrosilylation reactions.



(3).



(tpy)Br₂] (Entry 3). Since **9d** is generated from the reaction of **9s** with another molecule of acetophenone, the higher yield of **9d** than **9s** indicates that acetophenone reacts faster with **9s** than with Ph_2SiH_2 in this system. The mechanism through which **9d** production is favored over **9s** production is under investigation.

3.6. Hydrosilylation of acetophenone

It is well known that first-row transition metals often catalyze the hydrosilylation of ketones [4,12], which can facilitate the reduction of



(6).

ketones under mild conditions [13]. Therefore, ketone hydrosilylation catalyzed by $[M(tpy)Br_2]$ (Mn, Co, Ni, and Cu) was investigated and compared with olefin hydrosilylation. Acetophenone was selected as a model ketone substrate and treated with Ph₂SiH₂ in the presence of catalytic quantities of $[M(tpy)Br_2]$ and NaBHEt₃. The results are summarized in Table 6. Unlike in the case of 1-octene, all four complexes catalyzed hydrosilylation. The association constant of acetophenone to the active species of $[M(tpy)Br_2]$ is likely to be much higher than that of 1-octene owing to the strong oxophilicity of the first-row transition metals; this would explain the difference in reactivity between acetophenone and olefins.

In the reaction of 1:1 mixture of acetophenone and Ph₂SiH₂ catalyzed by [M(tpy)Br₂] (Eq. 6), the 2:1 (acetophenone:Ph₂SiH₂) double hydrosilylation product (**9d**) was surprisingly the major product (Table 6), although, in the case of [Mn(tpy)Br₂], the yields of **9d** and **9s** were approximately equal (Entry 1). A 1:1 single hydrosilylation product (**9s**) is usually predominant in the reaction of a 1:1 mixture of ketones and hydrosilanes [**4**,12]. To form **9d**, two hydrosilylation reactions are required; therefore, the TON should be two per molecule of **9d**. Thus, the total TON using [Mn(tpy)Br₂] was the highest, but the selectivity for **9d** was the lowest among the complexes shown in Table 6. The highest selectivity for **9d** was recorded for the reaction using [Ni

4. Conclusions

Co and Ni complexes bearing 2,2':6',2"-terpyridine, [Co(tpy)Br₂], and [Ni(tpy)Br₂], demonstrated catalytic activity for olefin (1-octene) hydrosilylation in the presence of NaBHEt₃ as a reducing activator, whereas [Mn(tpy)Br₂] and [Cu(tpy)Br₂] did not show such activity. [Co (tpy)Br₂] exhibited better catalytic activity than [Ni(tpy)Br₂]. The main product was a linear hydrosilvlation product, but a small amount of a branched hydrosilylation product was also produced. The generation of this by-product was suppressed by the addition of pyridine or THF. The catalytic system using [Co(tpy)Br₂] was applicable to hydrosilylations involving primary and tertiary silanes. On the other hand, for ketone (acetophenone) hydrosilylation, all complexes used in this study showed catalytic activity. The 1:2 (Ph2SiH2:acetophenone) double hydrosilvlation product (9d) was the main product, even in the reaction of a 1:1 mixture of acetophenone and Ph₂SiH₂. Although the double hydrosilvlation product (9d) is expected from the stepwise hydrosilvlation of Ph₂SiH₂ through a single hydrosilylation product (9s), the yield of 9d was higher than that of 9s. The detailed reaction mechanism is still unclear, but it should be noted that the hydrosilylation of 1-octene with Ph₂SiH₂ catalyzed by [M(tpy)Br₂] did not produce the double hydrosilylation product Ph₂Si(C₈H₁₇)₂. This difference seems to be due to the

high oxophilicity of the first-row transition metals; the details are under consideration.

CRediT authorship contribution statement

Katsuaki Kobayashi: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Writing - original draft. Hiroshi Nakazawa: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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