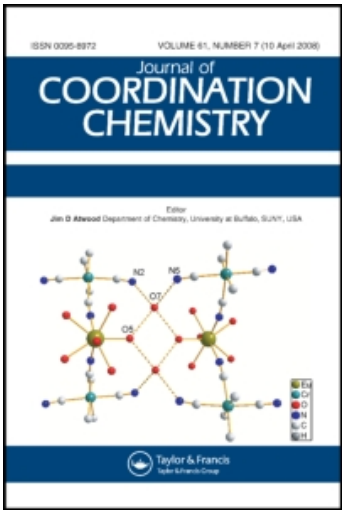

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Synthesis and catalytic properties of N-functionalised carbene complexes of rhodium(I)

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Synthesis and catalytic properties of *N*-functionalised carbene complexes of rhodium(I)

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Reaction of $[RhCl(COD)]_2$, with 1,3-dialkylimidazolinylidene (**1**) or 1,3-dialkylbenzimidazolinylidene (**2**) resulted in the formation of rhodium(I) 1,3-dialkylimidazolin-2-ylidene (**3a-c**) and 1,3-dialkylbenzimidazolin-2-ylidene (**4a,b**) complexes. Triethylsilane reacts with acetophenone derivatives in the presence of catalytic amounts of RhCl(COD)(1,3-dialkylimidazolin-2-ylidene) or RhCl(COD)(1,3-dialkylbenzimidazolin-2-ylidene) to give the corresponding silylethers in good yield (57–98%).

Keywords: Benzimidazolin-2-ylidene; Imidazolin-2-ylidene; *N*-heterocyclic carbene; Rhodium(I); Hydrosilylation

1. Introduction

An important goal in organic chemistry is the development of green processes that use fewer raw materials and less energy, maximize the use of renewable resources, and minimize or eliminate the use of dangerous chemicals. Clearly, none of this is possible without catalysis. The availability of catalysts to perform specific transformations is critical for both industry and research. Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behaviour of a variety of metal-containing systems. Advances in ligand design have allowed not only for improvements of known processes in terms of scope, mildness, and catalyst loadings, but also the discovery of new selective reactions. Coordination chemistry directed towards catalysis has been boosted in recent years by the discovery of *N*-heterocyclic carbenes as ligands [1].

Homogeneous organometallic catalysis has long depended on phosphine ligands [2, 3]. Despite their effectiveness in controlling reactivity and selectivity, phosphine catalysts require air-free handling to prevent the oxidation of the ligand and are subject

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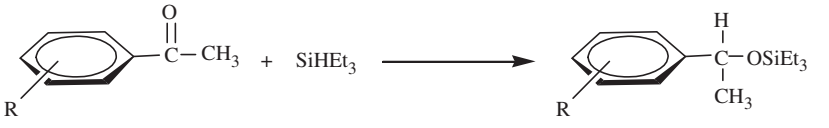
to P-C activation at elevated temperatures. Recently, nucleophilic *N*-heterocyclic carbenes (NHCs) [4], with stronger σ-donor electronic properties than bulky tertiary phosphines [5], have emerged as a new family of ligands. In contrast to metal complexes of phosphines, metal-NHC complexes appear to be extraordinarily stable towards heat, air and moisture due to the high dissociation energies of the metal-carbon bond [6]. Precursor imidazolium salts are often easier to obtain than phosphines but preparation of metal compounds from these salts can be difficult [7]. The most common method is direct complexation of free NHC, either isolated [8] or generated *in situ* [9] by deprotonation of imidazolium salts. These methods require that the free NHC be stable and may be complicated by the presence of other acidic protons in the ligand precursor. Oxidative addition of an imidazolinium carbon-hydrogen bond [10] to a low valency metal centre and addition of an electron-rich olefin with C=C bond cleavage [11] can also lead to metal-NHC complexes in certain cases. Recently, NHCs functionalised with classical heteroatom donors have been used as versatile multidentate spectators in a range of transition metal complexes. In this area we [12] and others [13] have reported *O*- and *N*-functionalised NHC complexes of Ru, Rh, Ir and Pd.

We have previously reported the use of an imidazolidin-2-ylidene, tetrahydropyrimidin-2-ylidene and tetrahydrodiazepin-2-ylidenepalladium(II) system, formed *in situ*, which exhibits high activity in various coupling reactions of aryl bromides and chlorides [14]. In order to obtain a more stable, efficient and active system, we have also investigated benzo-annelated derivatives [15]. Recently our group reported that novel complexes of rhodium(I) based on 1,3-dialkyimidazolidin-2-ylidenes give good yields for the addition of phenylboronic acid to aldehydes [16].

Hydrosilylation is an important industrial process which, *inter alia*, is used for the synthesis of polysiloxanes and polysilanes [17]. Moreover, it is applied to the reduction of ketones to secondary alcohols [18]. In general, the term hydrosilylation is used to describe an addition reaction of hydrosilanes to double and triple bonds and in the laboratory hydrosilylation is a very convenient method for the synthesis of a range of organosilicon compounds. The development of various hydrosilylation catalysts has been summarized [19].

Although rhodium-carbene complexes have been extensively studied, there are few reports on heir hydrosilylation reactions in rhodium-mediated processes [20]. Based on these findings and our continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could use the catalytic activity of rhodium-1,3-dialkylperhydrobenzimidazolin-2-ylidene and 1,3-dialkylimidazolin-2-ylidene complexes for the hydrosilylation of acetophenones (scheme 1). We report a straightforward preparation of new RhCl(COD)(1,3-dialkylbenzimidazolin-2-ylidene) and RhCl(COD)(1,3-dialkylimidazolin-2-ylidene) complexes andtheir efficient catalysis of the hydrosilylation of acetophenones.



Scheme 1. Hydrosilylation of acetophenones.

2. Experimental

All reactions for the preparation of **1–4** were carried out under Ar in flame-dried glassware using standard Schlenk flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). Flash chromatography: Merck silica gel 60 (230–400 mesh). The complex $[RhCl(COD)]_2$ [21] and **1** and **2** were prepared according to known methods [22]. All reagents were purchased from Aldrich. All ^1H and ^{13}C NMR measurements were performed in $CDCl_3$. NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H) or 100 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS; coupling constants (J) are in Hz. IR spectra were recorded using KBr pellets in the range 400–4000 cm^{-1} on a ATI UNICAM 1000 spectrophotometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by the Turkish Resarch Council (Ankara, Turkey) Microlab.

2.1. *General procedure for the preparation of the rhodium-carbene complexes (3a–c, 4a–b)*

A solution of 1,3-dialkylimidazolinylidene (**1**) or 1,3-dialkylbenzimidazolinylidene (**2**) (0.40 mmol) and $[RhCl(COD)]_2$ (0.40 mmol) in toluene (15 cm^3) was heated under reflux for 2 h. Upon cooling to room temperature, yellow-orange crystals of **3a–c**, **4a–b** were obtained. The crystals were filtered off, washed with diethylether (3×15 cm^3) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2/Et_2O.

2.1.1. Chloro(η^4-1,5-cyclooctadiene){1,3-*bis*(4-picolyl)imidazolin-2-ylidene}rhodium(I), (3a). Yield: 0.29 g (72%), m.p.: 242–243°C, IR $\nu_{(NCN)}$: 1500 cm^{-1}. Anal. Calcd for $C_{23}H_{28}N_4ClRh$ (%): C, 55.36; H, 5.62; N, 11.23. Found: C, 55.41; H, 5.56; N, 11.29. ^1H NMR (δ, $CDCl_3$): 3.37 (m, 4H, NCH_2CH_2N), 5.61, 5.71 (d, 4H, $J_{HH} = 15.2$ Hz, $CH_2C_5H_4N$), 7.45, 8.65 (d, 8H, $J_{HH} = 5.6$ Hz, $J_{HH} = 6.4$ Hz, $CH_2C_5H_4N$), 5.05 (s, 4H, CH_{COD}), 1.89, 2.20 (m, 8H, CH_{2COD}). ^1C {H} NMR (δ, $CDCl_3$): 216.0 (d, $J = 47.2$ Hz, $C_{carbene}$), 48.5 (NCH_2CH_2N), 53.9 ($CH_2C_5H_4N$), 123.4, 145.7, 150.8 ($CH_2C_5H_4N$), 69.1, 101.0 (d, $J = 14.5$ Hz, $J = 6.1$ Hz, CH_{COD}), 28.8, 31.1 (CH_{2COD}).

2.1.2. Chloro(η^4-1,5-cyclooctadiene){1,3-*bis*(2-diisopropylaminoethyl)imidazolin-2-ylidene} rhodium(I), (3b). Yield: 0.39 g (83%), m.p.: 165–166°C, IR $\nu_{(NCN)}$: 1504 cm^{-1}. *Anal.* Calcd for $C_{27}H_{52}N_4ClRh$ (%): C, 56.78; H, 9.18; N, 9.81. Found: C, 56.71; H, 9.05; N, 9.75. ^1H NMR (δ, $CDCl_3$): 3.49, 4.30 (m, 4H, NCH_2CH_2N), 3.61 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 2.60, 2.94 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 3.07 (sep, 2H, $J_{HH} = 6.4$ Hz, $NCH(CH_3)_2$), 1.09 (d, 12H, J_{HH}=2.8 Hz, $NCH(CH_3)_2$), 3.28, 4.92 (d, 4H, J_{HH}=3.2 Hz CH_{COD}), 1.88, 2.30 (m, 8H, CH_{2COD}). ^1C {H} NMR (δ, $CDCl_3$): 211.2 (d, $J = 44.2$ Hz, $C_{carbene}$), 48.5 (NCH_2CH_2N), 50.8 ($CH_2CH_2N(Pr^i)_2$), 42.8 ($CH_2CH_2N(Pr^i)_2$), 48.1 ($NCH(CH_3)_2$), 19.8, 19.9 ($NCH(CH_3)_2$), 67.1, 97.7 (d, $J = 13.7$ Hz, $J = 6.1$ Hz, CH_{COD}), 27.6, 31.8 (CH_{2COD}).

2.1.3. Chloro(η^4-1,5-cyclooctadiene){1,3-*bis*(6-methyl-2-picolyl)imidazolin-2-ylidene} rhodium(I), (3c). Yield: 0.33 g (78%), m.p.: 192–194°C, IR $\nu_{(NCN)}$: 1511 cm^{-1}. Anal. Calcd for $C_{25}H_{32}N_4ClRh$ (%): C, 56.99; H, 6.12; N, 10.63. Found: C, 56.92; H, 6.18; N, 10.67. ^1H NMR (δ, $CDCl_3$): 3.37, 3.54 (m, 4H, NCH_2CH_2N), 5.22, 5.78 (d, 4H, J_{HH}=15.2 Hz, $CH_2C_5H_4N(CH_3)$-6), 2.54 (s, 3H, $CH_2C_5H_4N(CH_3)$-6), 7.06 (d, 4H, J_{HH}=7.6 Hz, $CH_2C_5H_3N(CH_3)$-6), 7.60 (m, 2H, $CH_2C_5H_3N(CH_3)$-6), 3.47, 4.99 (d, 4H, J_{HH}=7.2 Hz, CH_{COD}), 1.88, 2.29 (m, 8H, CH_{2COD}). ^1C {H} NMR (δ, $CDCl_3$): 212.7 (d, J = 47.3 Hz, $C_{carbene}$), 47.6 (NCH_2CH_2N), 55.5 ($CH_2C_5H_4N(CH_3)$-6), 23.4 ($CH_2C_5H_4N(CH_3)$-6), 118.7, 121.1, 127.7, 136.3, 137.6, 149.4, 150.0, 156.5, 156.9, 157.2 ($CH_2C_5H_3N(CH_3)$-6), 67.9, 98.5 (d, J = 14.5 Hz, J = 6.9 Hz, CH_{COD}), 27.7, 31.7 (CH_{2COD}).

2.1.4. Chloro(η^4-1,5-cyclooctadiene){1,3-*bis*(2-diisopropylaminoethyl)benzimidazolin-2-ylidene}rhodium(I), (4a). Yield: 0.44 g (88%), m.p.: 108–110°C, IR $\nu_{(NCN)}$: 1473 cm^{-1}. Anal. Calcd for $C_{31}H_{52}N_4ClRh$ (%): C, 60.14; H, 8.47; N, 9.05. Found: C, 60.01; H, 8.41; N, 9.12. ^1H NMR (δ, $CDCl_3$): 7.20, 7.31 (m, 4H, NC_6H_4N), 3.27, 4.31 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 2.76, 3.27 (m, 4H, $CH_2CH_2N(Pr^i)_2$), 3.17 (sep, 2H, J_{HH}=6.4 Hz, $NCH(CH_3)_2$), 1.09, 1.21 (d, 12H, J_{HH}=4.0 Hz, $NCH(CH_3)_2$), 5.10, 5.13 (d, 4H, J_{HH} = 6.0 Hz CH_{COD}), 1.96, 2.43 (m, 8H, CH_{2COD}). ^1C {H} NMR (δ, $CDCl_3$): 196.5 (d, J = 49.6 Hz, $C_{carbene}$), 109.9, 122.4, 135.0 (NC_6H_4N), 50.5 ($CH_2CH_2N(Pr^i)_2$), 44.7 ($CH_2CH_2N(Pr^i)_2$), 50.3 ($NCH(CH_3)_2$), 21.4, 21.5 ($NCH(CH_3)_2$), 68.9, 100.3 (d, J = 13.8 Hz, J = 6.1 Hz, CH_{COD}), 28.8, 33.1 (CH_{2COD}).

2.1.5. Chloro(η^4-1,5-cyclooctadiene){1-(2-metoksiethyl)-3-(2-diisopropylaminoethyl) benzimidazolin-2-ylidene}rhodium(I), (4b). Yield: 0.37 g (85%), m.p.: 112–114°C, IR $\nu_{(NCN)}$: 1475 cm^{-1}. Anal. Calcd for $C_{26}H_{41}N_3OClRh$ (%): C, 56.75; H, 7.51; N, 7.64. Found: C, 56.66; H, 7.62; N, 7.55. ^1H NMR (δ, $CDCl_3$): 7.19, 7.30 (m, 4H, NC_6H_4N), 4.27, 4.88 (m, 2H, $CH_2CH_2N(Pr^i)_2$), 2.31, 2.77 (m, 2H, $CH_2CH_2N(Pr^i)_2$), 3.25 (sep, 1H, J_{HH} = 6.0 Hz, $NCH(CH_3)_2$), 1.19, 1.21 (d, 6H, J_{HH} = 2.4 Hz, $NCH(CH_3)_2$), 4.19 (m, 2H, $CH_2CH_2OCH_3$), 5.08 (t, 2H, J_{HH} = 6.4 Hz, $CH_2CH_2OCH_3$), 3.35, 3.37 (s, 3H, $CH_2CH_2OCH_3$), 3.33, 5.16 (d, 4H, J_{HH} = 5.6 Hz CH_{COD}), 2.0, 2.48 (m, 8H, CH_{2COD}). ^1C {H} NMR (δ, $CDCl_3$): 196.7 (d, J = 49.5 Hz, $C_{carbene}$), 109.6, 111.2, 122.4, 122.5, 134.9, 135.6 (NC_6H_4N), 50.4 ($CH_2CH_2N(Pr^i)_2$), 44.9 ($CH_2CH_2N(Pr^i)_2$), 50.3 ($NCH(CH_3)_2$), 21.4, 21.6 ($NCH(CH_3)_2$), 48.9 ($CH_2CH_2OCH_3$), 71.9 ($CH_2CH_2OCH_3$), 59.3 ($CH_2CH_2OCH_3$), 68.9, 100.4 (d, J = 14.5 Hz, J = 3.8 Hz, CH_{COD}), 28.6, 29.1, 32.8, 33.4 (CH_{2COD}).

2.2. *General procedure for rhodium-carbene catalyzed addition of acetophenone to triethylsilane*

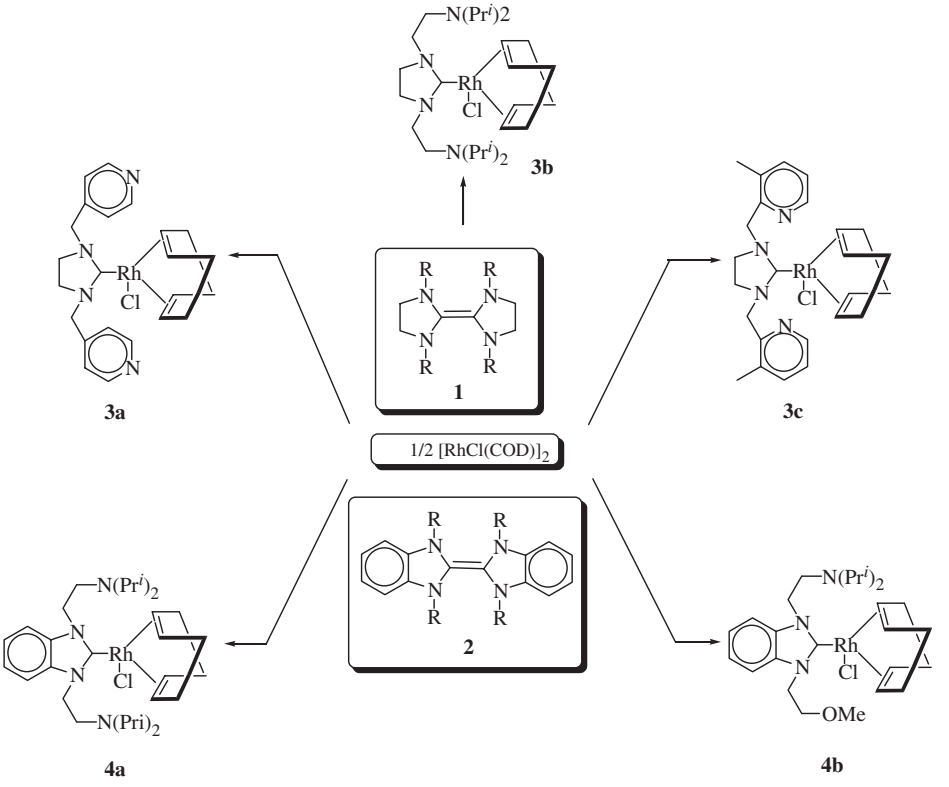
Acetophenone (1 mmol), triethylsilane (1.25 mmol) and rhodium carbene catalyst (0.5 mol% based on ketone) were placed in a Schlenk tube. The resulting mixture was heated for 2h at 90°C, cooled to ambient temparature, and purified by flash chromatography (hexane/ethyl acetate, 10/1). Analysis of the reaction product was carried out by NMR spectroscopy and GC.

3. Results and discussion

3.1. *Synthesis and characterisation of RhCl(COD)NHC*

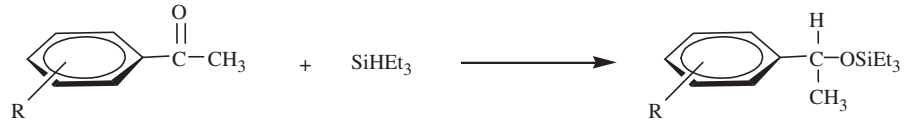
Bis(1,3-dialkylimidazolin-2-ylidene) (**1**) and *bis*(1,3-dialkylbenzimidazolin-2-ylidene) (**2**), were synthesised using a method similar to that reported by Lappert *et al*. [22]. Reaction of (**1**) or (**2**) with $[RhCl(COD)]_2$ proceeded smoothly in refluxing toluene to give RhCl(COD)(1,3-dialkylimidazolin-2-ylidene) (**3a,c**) or RhCl(COD)(1,3-dialkylbenzimidazolin-2-ylidene) complexes (**4a,b**) as crystalline solids (scheme 2). Each rhodium compound was fully characterized by ^{1}H and ^{13}C NMR spectroscopy, FT-IR, and elemental analysis.

The rhodium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1473–1511 cm^{-1} [23]. ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ lie in the range 196.5–216.0 ppm and are similar to those found for other carbene complexes. Coupling constants $J(^{103}Rh\text{-}^{13}C)$ for the rhodium complexes (**3**) and (**4**) are comparable with those found for other carbene rhodium(I) complexes. The complexes diplay typical spectroscopic signatures which are in line with those recently reported for RhCl(COD)(1,3-dialkylimidazolin-2-ylidine) complexes [23].



Scheme 2. Synthesis of rhodium-carbene complexes (**3a,c** and **4a,b**).

Table 1. Hydrosilylation of acetophenone derivatives.



	R	Catalyst	Yield[a] (%)
1	H	**3a**	82
2	H	**3b**	75
3	H	**3c**	88
4	H	**4a**	97
5	H	**4b**	80
6	*o*-OMe	**3a**	93
7	*o*-OMe	**3b**	80
8	*o*-OMe	**3c**	95
9	*o*-OMe	**4a**	98
10	*o*-OMe	**4b**	96
11	*m*-OMe	**3a**	94
12	*m*-OMe	**3b**	78
13	*m*-OMe	**3c**	97
14	*m*-OMe	**4a**	98
15	*m*-OMe	**4b**	97
16	*p*-Cl	**3a**	57
17	*p*-Cl	**3b**	65
18	*p*-Cl	**3c**	60
19	*p*-Cl	**4a**	72
20	*p*-Cl	**4b**	70

[a]Reaction conditions: 1.0 mmol of acetophenone, 1.25 mmol of triethylsilane, 0.5 mmol% (based on ketone) **3** or **4**, T = 80°C, 2 h; purity of compounds checked by GC; yields are based on ketone.

3.2. *Hydrosilylation of acetophenone derivatives*

Hydrosilylation reactions involve the addition of inorganic or organic silicon hydrides to multiple bonds such as alkyne, alkene, ketoxime and carbonyl groups. Metal complexes are able to catalyze hydrosilylation of organic substrates under mild conditions and are very attractive for many processes. We have observed that Rh(I) complexes of 1,3-dialkylimidazolin-2-ylidene and 1,3-dialkylbenzimidazolin-2-ylidene can be used as effective catalysts for the hydrosilylation of acetophenone derivatives. Rhodium-NHC complexes (**3**) and (**4**) are active catalysts for the hydrosilylation of acetophenone derivatives and the addition of triethylsiliane to acetophenone proceeds in high yield and quite rapidly, even with a low catalyst loading. All reactions were carried out without any special need for inert conditions, since the catalysts used proved to be fairly stable under an oxygen-containing atmosphere, even at high temperatures. Results are summarized in table 1. Under these conditions, acetophenone, 2-methoxyacetophenone, 3-methoxyacetophenone, and 4-chloroacetophenone react very cleanly with triethylsilane in good yields (table 1, entries 4, 9, 14 and 19). These results are in agreement with other reports on rhodium-carbene catalyzed hydrosilylation of carbonyl compounds [20a, f].

In summary, *N*-functionalised rhodium-carbenes have been prepared from the readily available starting materials *bis*(1,3-dialkylimidazolin-2-ylidene) and *bis*(1,3-dialkylbenzimidazolin-2-ylidene) and characterized. Their hydrosilylation activity with

acetophenone derivatives resulting in the formation of corresponding silylethers has been shown to be effective. Studies of the reactivity of the complexes, extension of the methodology to other transition metals and the synthesis of other functionalised *N*-heterocyclic carbene ligands with a variety of other donor functionalities is continuing.

Acknowledgements

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