# Catalytic C–H/olefin coupling

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Abstract - Several ruthenium complexes have been found to
catalyze the addition of the C-H bond of arenes to olefins. Phenyl
methyl ketone undergoes addition at its ortho position across
the double bond of trimethylvinylsilane in the presence of a
catalytic amount of $RuH_2(CO)(PPh_3)_3$ to give 1 : 1 and 1 : 2
coupling products. In the latter, the two ortho hydrogens have
reacted. Similarly, 2-methylphenyl methyl ketone reacts with
trimethylvinylsilane and triethoxyvinylsilane to give the
corresponding 1 : 1 coupling products in virtually quantitative
yields. The results represent a breakthrough in the chemistry of
carbon-hydrogen bond cleavage by metal complexes.

INTRODUCTION

In this paper we disclose an efficient catalytic reaction that enables the addition of
arenes to olefins. This discovery represents a breakthrough in the chemistry of C-
H bond cleavage by metal complexes, a field that has been under intense study
since 1963 when Kleiman and Dubeck reported a C-H bond cleavage of azobenzene
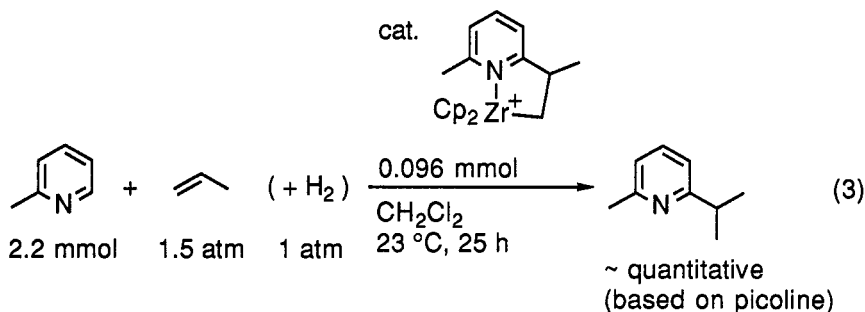by reaction with a nickel complex (eq 1).[1]

$$Cp_2Ni \quad + \qquad \longrightarrow \qquad \qquad (1)$$
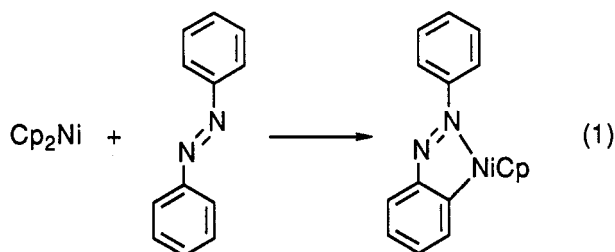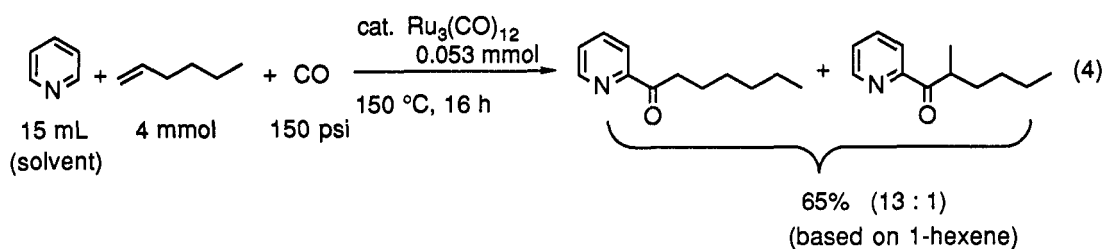
Chatt and Davidson subsequently observed in 1965 an oxidative addition to a C-H
bond of naphthalene with a Ru(0) complex generated in situ by the reduction of a
Ru(II) complex with sodium naphthalenide, as shown in eq 2.[2]

(2)
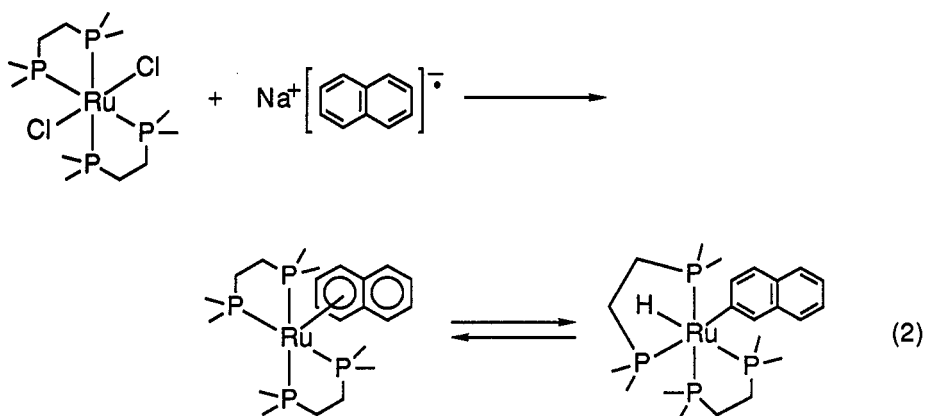
The crystal structure of RuCl₂(PPh₃)₃ determined by La Placa and Ibers in 1965 showed that the ruthenium was in the center of an octahedron containing the five ligands; the last coordination site being occupied by an ortho-hydrogen of one of the PPh₃ ligands.[3] This observation clearly demonstrated that there can exist a nonclassical interaction between a bonded hydrogen atom and a transition metal.

Prompted by these observations, numerous studies have been carried out ever since. C-H bond cleavage by metals has now been established as a common phenomenon in stoichiometric reactions. Various interesting catalytic reactions involving C-H bond cleavage have also been reported but with a limited degree of success from the view point of organic synthesis. More than fifty review articles in this field have appeared.[4]
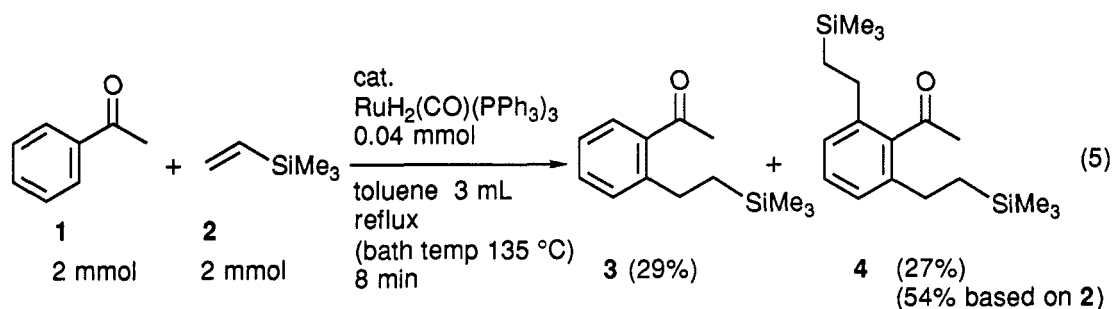
Notable advances in catalytic reactions reported recently are those of Jordan and Taylor (eq 3)[5] and Moore and co-workers (eq 4).[6] In both cases, a new carbon-carbon bond is formed from pyridines in exceptionally high yields. However, in the reaction 3 the use of hydrogen was necessary to obtain higher yield, which in turn resulted in consumption of the olefin by hydrogenation. In the latter (eq 4), a large excess amount of pyridine was used.

cat.

$$Cp_2Zr^+$$

(3)

2.2 mmol   1.5 atm   1 atm

0.096 mmol
CH₂Cl₂
23 °C, 25 h

~ quantitative
(based on picoline)

$$\text{(4)}$$

15 mL 4 mmol 150 psi
(solvent)

65% (13 : 1)
(based on 1-hexene)

RESULTS[7]

A remarkable catalytic reaction involving C–H bond cleavage has been found. By this reaction the C–H bond at the ortho position of aromatic ketones can be added across the double bond of olefins. The catalytic C–H/olefin coupling begins with cyclometalation of an aromatic ketone with a Ru(0) complex followed by interception of the thus formed intermediate to give the addition product after reductive elimination (vide infra).

The reaction of phenyl methyl ketone (**1**) with trimethylvinylsilane (**2**) has been found to proceed in the presence of a catalytic amount of ruthenium complexes (eq 5). For example, when a mixture of **1** (2 mmol), **2** (2 mmol), and $RuH_2(CO)(PPh_3)_3$ (0.04 mmol) was vigorously refluxed in 3 mL of toluene for several minutes, a 1 : 1 coupling product **3** and a 1 : 2 coupling product **4** were obtained in 29% and 27% yields based on **1**, respectively (eq 5). The yield of **4** was 54% based on **2**.
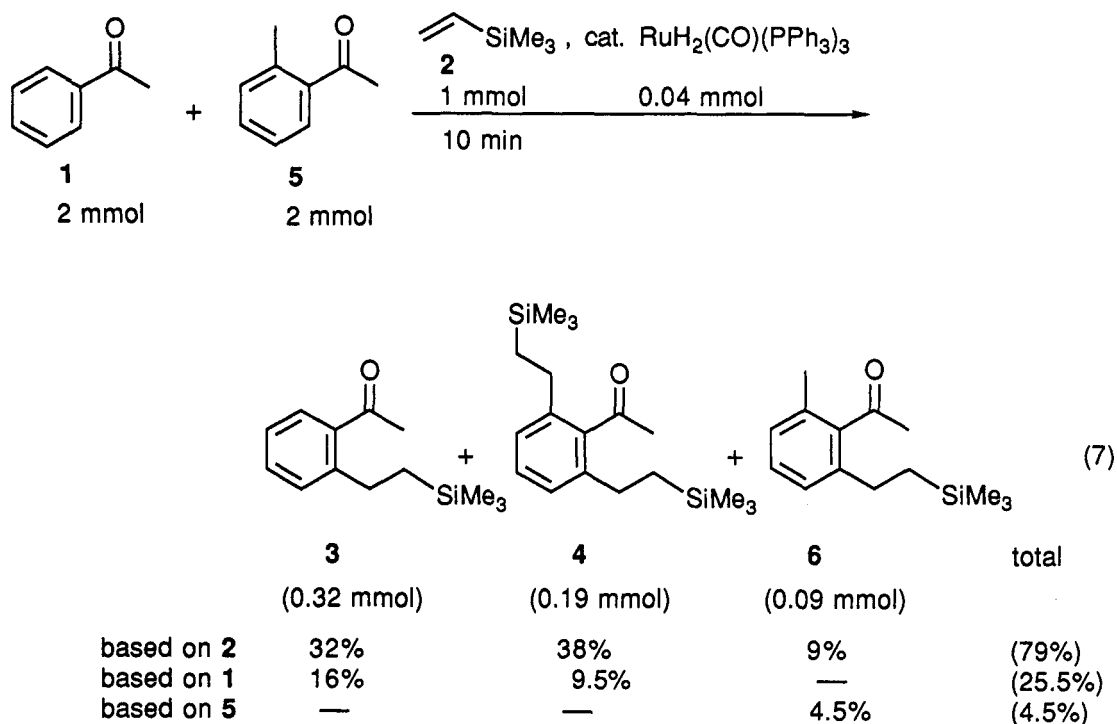
$$\text{(5)}$$

1   2
2 mmol 2 mmol

cat.
$RuH_2(CO)(PPh_3)_3$
0.04 mmol

toluene 3 mL
reflux
(bath temp 135 °C)
8 min

3 (29%)   4 (27%)
(54% based on 2)

Among the ruthenium complexes examined for their catalytic activities, $RuH_2(CO)(PPh_3)_3$ and $Ru(CO)_2(PPh_3)_3$ were the most effective in catalyzing the reaction of eq 5. Similar ruthenium complexes such as $RuH_2(PPh_3)_4$ and $Ru(CO)_3(PPh_3)_2$ were fairly effective, while $RuHCl(CO)(PPh_3)_3$, $RuCl_2(PPh_3)_3$, $RuCl_2(CO)_2(PPh_3)_2$, $RuCl(OAc)(CO)(PPh_3)_2$, and $Ru_3(CO)_{12}$ did not show any catalytic activity for the reaction 5 under the reaction conditions described above. Although the ruthenium complex $RuCl(OAc)(CO)(PPh_3)_2$ is known to react with phenyl methyl ketone to give an orthoruthenation product as the result of C–H bond cleavage (vide infra),[8] it is not effective as a catalyst for the above reaction.
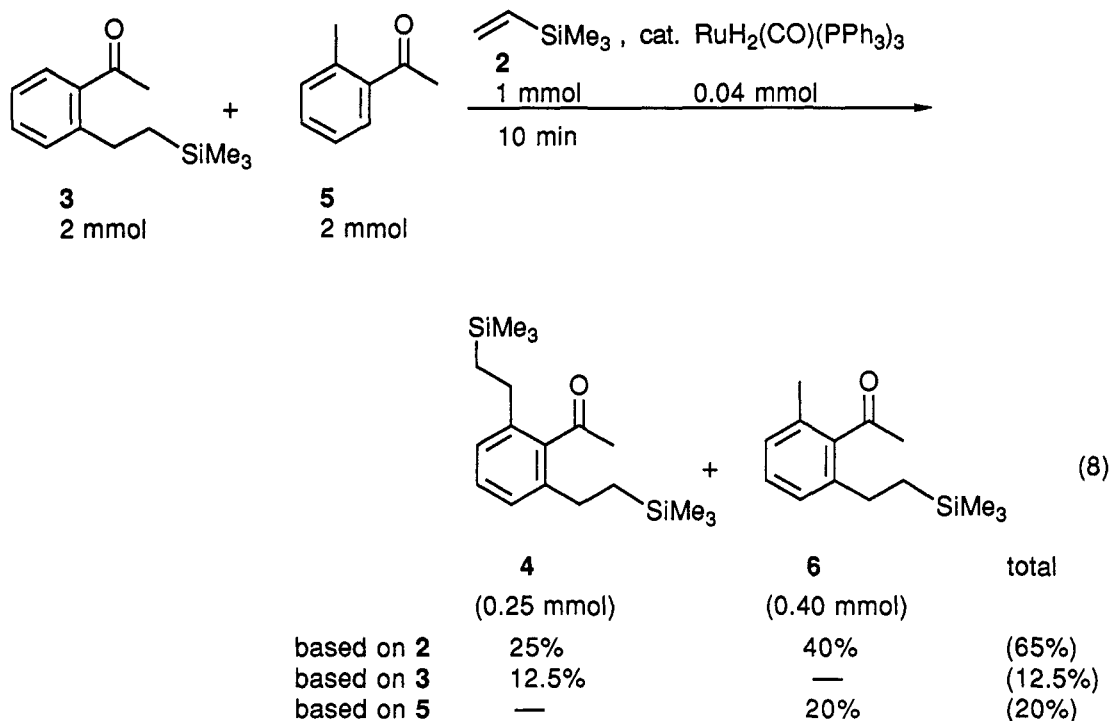
To avoid complexity, 2-methylphenyl methyl ketone (**5**) was examined as the ketone component to prevent formation of the 1 : 2 coupling product. The catalytic reaction of **5** with two equivalents of **2** gave the coupling product **6** almost quantitatively (eq 6).
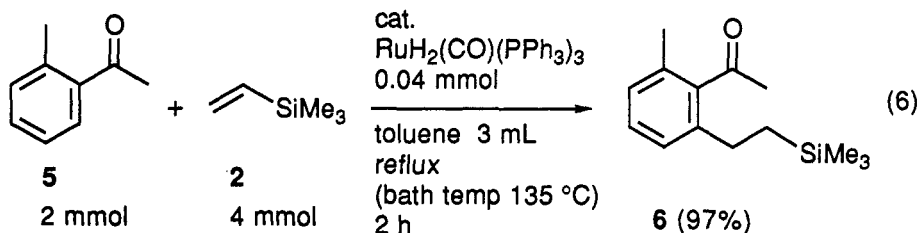
We were interested in the difference in the reaction time required for consumption of the aromatic ketones in the reactions 5 and 6. Particularly, the rate of formation of **4** seemed to be much greater than **6**. The results of experiments described below imply that coordination of the carbonyl group of the ketone to the ruthenium is important.

Two competitive reactions were carried out as shown in eqs 7 and 8.

	3	**4**	**6**	total
	(0.32 mmol)	(0.19 mmol)	(0.09 mmol)	
based on 2	32%	38%	9%	(79%)
based on 1	16%	9.5%	—	(25.5%)
based on 5	—	—	4.5%	(4.5%)

|	4	6	total
	(0.25 mmol)	(0.40 mmol)	
based on 2	25%	40%	(65%)
based on 3	12.5%	—	(12.5%)
based on 5	—	20%	(20%)

Under the reaction conditions shown above, a mixture of **1** and **5** reacted with an insufficient amount of the olefin **2** to give three products, **3**, **4**, and **6** (eq 7). Yields based on each starting material are shown in the eq 7. The 1 : 2 coupling product **4** seemed to be produced by further reaction of the 1 : 1 coupling product **3**, but this is only partly true as will be described below. Similarly a mixture of equal amounts of **3** (the plausible intermediate for the formation of **4**) and **5** reacted with an insufficient amount of **2** to afford **4** and **6** in the yields given in eq 8. The relative rate of consumption of **1**, **5**, and **3** are estimated to be 9 : 1.6 : 1, as calculated from the consumption of **1** 25.5% in eq 7, **5** 4.5% in eq 7, **5** 20% in eq 8, and **3** 12.5% in eq 8. These relative rates indicate that introduction of an alkyl group to the phenyl ring retards significantly the rate of the catalytic reaction. Of note is the formation of an unexpectedly large amount of **4** in reaction 7. Assuming that all of **4** is formed via **3** in reaction 7, the yield of **4** in eq 7 should not exceed 2.8% (= 4.5 X (12.5/20)) as estimated from the relative rates of formation of **4** and **6** in eq 8. Actually, however, the yield of **4** in eq 7 is 9.5% and the above assumption is obviously not correct. At least 6.7% yield (= 9.5 - 2.8) of **4** in eq 7 must have been produced by a route not involving **3**. We suggest that the major portion of the product **4** is formed from **1** without decomplexation of the carbonyl group of **3** from ruthenium throughout the reaction. This leads to estimation that at least 71% (= (6.7/9.5) X 100) of **4** is formed by the route not involving "free **3**" and 29% of **4** from once liberated "free **3**", in reaction 7. The course of the catalytic reaction is depicted in Scheme I.

Scheme I
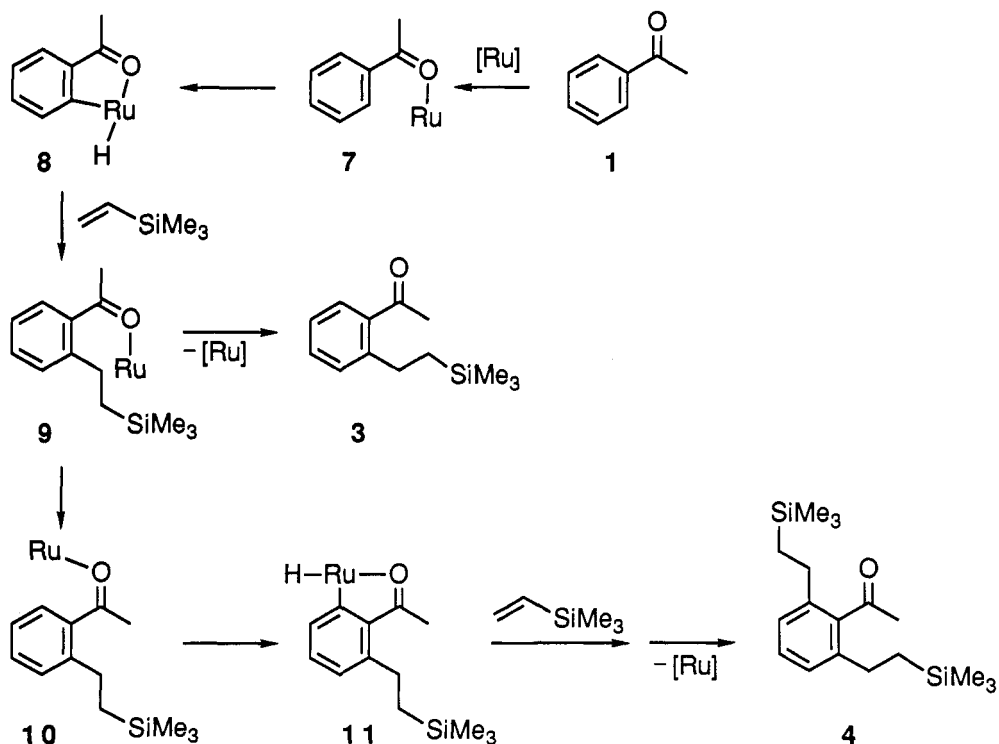
For simplicity, possible equilibria are not included in Scheme I. Coordination of the carbonyl oxygen (**1** to **7**) is important to direct the ruthenium metal close to the C-H bond to be cleaved. Thus formed ruthenium hydride complex **8** undergoes olefin coordination and migratory insertion followed by reductive elimination to afford **9**, i.e., **3•Ru** complex. Decomplexation affords **3**. On the other hand, carbon-carbon bond rotation (**9 → 10**) directs the ruthenium metal close to the other ortho C-H bond. Cleavage of this second C-H bond results in the formation of intermediate **11**. The cyclometalated complex **11** reacts with a second molecule of vinylsilane to afford the 1 : 2 coupling product **4**. Interestingly, the above results indicate that decomplexation of the ketone ligand from the metal is competitive with C-H bond cleavage. In other words, in the present reaction the rate of C-H bond cleavage is of the order of that for decomplexation of a ketone ligand. As described above, the reaction of mono-alkylphenyl ketone, **4** or **5**, was much slower than unsubstituted one **1**. This can be attributed to the steric repulsion between the ketonic methyl group and the alkyl group in the phenyl ring in the form such as **10** or **11**.

The mechanism of the present reaction is far from clear at the present time. That shown in Scheme I neglects many important steps. Much work remains to be done to solve the intriguing questions raised by the present discovery. It is noteworthy that cyclometalated complexes such as **12**,[8] **13**,[9] and **14**[10] structurally similar to **8** have been reported.

12   **13**   **14**
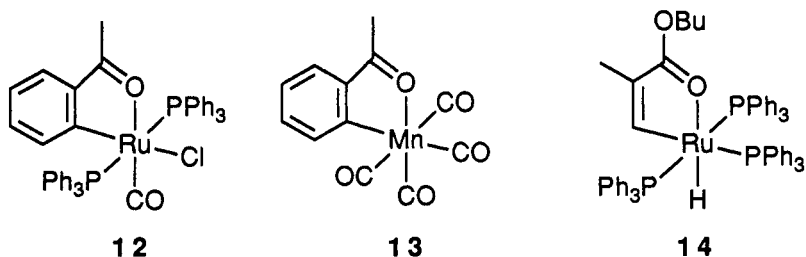
The vinylsilane **2** was less than ideal in the present reaction since its boiling point (bp 55 °C) is much lower than the reaction temperature. The use of a higher boiling vinylsilane **15** (bp 160 °C) gave the most impressive result even when equimolecular amounts of reactants were used (eq 9). The reaction was so clean that the initial GLC peaks of reactants, **5** and **15** disappeared after two hours and only a single new GLC peak for the 1 : 1 couping product **16** appeared (93% GLC yield). The reaction is operationally simple; mix the reagents and reflux. Isolation procedures are also straightforward. Evaporation of the solvent and bulb-to-bulb distillation allowed isolation of the pure product **16** (~ 90% yield) that gave correct elemental analysis data.
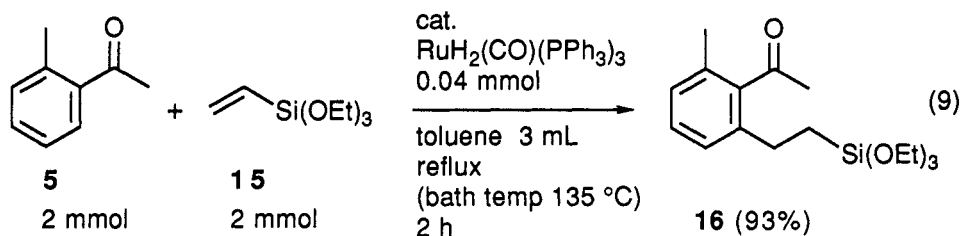
OUTLOOK

We are extending the present discovery in various directions. The new catalytic reaction can be applied to various carbonyl compounds and to various olefins. The results[7] indicate that catalytic reactions involving C-H bond cleavage by transition metals are now reaching the level required for practical organic synthesis with respect to efficiency, selectivity, and generality, for the first time since the initial discoveries made thirty years ago.[1-4]

In addition, the concept of interception of cyclometalated intermediates will become a powerful methodology for the development of new catalytic reactions. These results will be reported in due course.

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