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Rh(III)-Catalyzed Distal C-H Alkenylation of Weakly Coordinating Acetamides Via Desilylation Pathway

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Abstract. Rh(III)-Catalyzed distal *ortho*-C-H alkenylation of arylacetamides have been reported employing acetamide, a weak coordinating group, as a directing group. This challenging C-H alkenylation of arylacetamides has been achieved by using arylalkynyl silanes as a surrogate for terminal alkynes under redox neutral process through desilylation pathway. The control experiments suggest that the *in situ* generated Rh-species is likely to be Lewis acidic, which is playing a vital role in the desilylation step.

Keywords: Rhodium; acetamide; alkynyl silane; alkenylation; desilylation; C-H activation

Directed functionalization is opening up a number of new avenues for late-stage functionalization of organic molecules.[1] In the past decade, high-valent metal-catalyzed (Cp*M, M = Ru, Rh, Co, Ir) C-H bond activation/functionalization reactions have received tremendous attention in directing group strategy as they offer high reactivity, atom- and step-economical processes under ambient conditions.[1] Functionalized arylacetamides and arylacetic acids are essential structural motifs in many biologically active molecules.[2,3] Proximal *ortho*-C-H functionalization of arylbenzamides is a well-explored area under Cp*M catalyst systems.[4] Arylacetamides are challenging substrates for the distal C-H bond functionalization using a directing group strategy due to (i) the intrinsic ability of the arylacetamide to undergo tautomerization, (ii) the formation of unfavorable six-membered metallacycle, and (iii) the weak coordinating ability of acetamide group. The pioneering work by Yu[5] marks the beginning of distal C-H bond functionalization of arylacetamides using Pd-catalyst, which was persuaded by others.[6] Nevertheless these reactions require a stoichiometric or super stoichiometric amount of oxidants or special ligands. Generally, Cp*M-catalysed C-H activation reactions proceed via a concerted metalation-deprotonation pathway, which does not require a terminal oxidant, unless the overall process is an oxidative one.[1] However, the distal C-H functionalization of arylacetamides using high-valent (Cp*M) transition metal catalysts are scarce. Very recently, Ackermann has reported a distal *ortho*-alkenylation of arylacetamides by employing acrylates (activated olefins) and internal alkynes as alkene sources.[3]

Alkenes are important functional groups, which are susceptible to further synthetic manipulations. Most of the directed C-H alkenylation reactions using alkynes were accomplished by utilizing ainternal alkynes[7-9] as alkene sources under redox-neutral conditions, whereas compatibility of terminal alkynes for the similar transformation is limited due to the presence of relatively acidic proton.[10] Besides terminal alkynes are well-known to undergo homo coupling reaction in the presence of transition metal catalysts. Generally, Cp*Co(III)-catalytic systems are quite reactive with terminal alkynes to furnish the corresponding di-substituted olefin derivatives,[10] whereas the similar transformation with Cp*Rh(III)-catalytic systems is rare.[11] This incompatibility of terminal alkynes with Cp*Rh(III)-catalysts diminishes their synthetic potential in directing group chemistry. Finding an alternate for terminal alkynes is highly desirable which remains a challenge. In continuation of our interest in directing group chemistry,[12] herein we disclose a distal C-H bond alkenylation of arylacetamides in the presence of Cp*Rh(III)-catalyst. This reaction proceeds via a desilylation route, wherein arylalkynyl silanes are successfully utilized as surrogates for terminal alkynes.

We began our initial studies to investigate the compatibility of terminal alkynes[10] and its synthetic equivalents.[13,14] The reaction of arylacetamide **1a** with phenylacetylene under C-H activation conditions, with Rh-, Ru-, and Co-catalysts, the expected *ortho*-alkenylated aryl acetyamide **3aa** was not detected (Scheme 1a and see the SI, Table SI-1). As arylalkynyl carboxylic acids can also be used as a surrogate for terminal alkynes,[14] the reaction of **1a** with phenylpropiolic acid in the presence of Rh-, Ru-,

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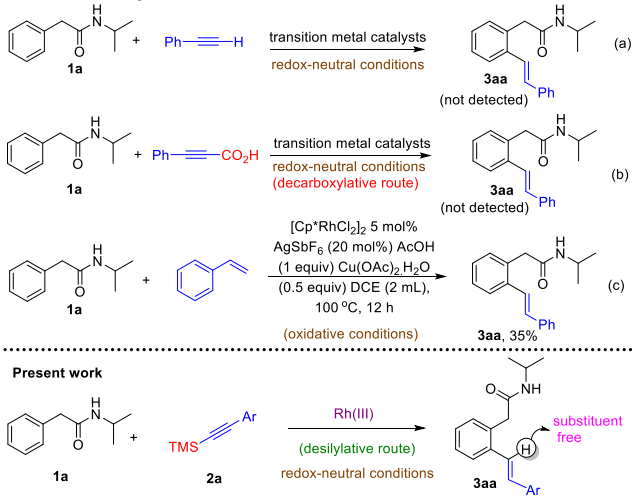
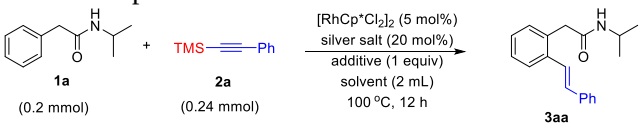
Scheme 1. Studies on the compatibility of phenylacetylene and its synthetic equivalents for *ortho* alkenylation of acetamides.



and Co-catalysts were performed. However, these reactions did not lead to the expected alkenylation product **3aa** (Scheme 1b and see SI, Table-SI-2). Next, the reaction of styrene with arylacetamide **1a** in the presence of Rh(III)-catalyst under oxidative conditions, furnished the expected *ortho*-akenylated product **3aa** in 35% yield (Scheme 1c). However, the yield of the product **3aa** could not be improved beyond 35% (for details see the SI, Table-SI-3).

As oxidative process often requires a stoichiometric amount of metal oxidants and leads to the formation of a large amount of metal waste in the large scale synthesis, we turned our attention to find another surrogate for terminal alkynes under redox-neutral process.[13] To our delight, the reaction of phenylalkynyl silane **2a** (0.24 mmol), with arylacetamide **1a** (0.2 mmol) in the presence of $[RhCp^*Cl_2]_2$ (5 mol%) as a catalyst, $AgSbF_6$ (20 mol%) as an activator, and $AdCO_2H$ (1 equiv) as an additive in DCE (2 mL) at 100 °C for 12 h, furnished the expected product **3aa** in 50% yield (Table 1, entry 1). It is worth noting that the product **3aa** was obtained through desilylation route. Since phenylalkynyl silane **2a** has furnished a better yield of **3aa** than styrene, further optimization studies were carried out using phenylalkynyl silane **2a** as a coupling partner. The solvent screening studies revealed that 1,2-dichloroethane (DCE) is a suitable solvent for this reaction (entries 1-4). Changing the additives from $AdCO_2H$ to PivOH improved the yield of the product **3aa** to 55%, whereas AcOH brought a slight dip in the yield of **3aa** to 44% (entries 5 and 6). The reaction using NaOAc as an additive was not useful as the product **3aa** was not detected in the reaction (entry 7). Changing the activator to $AgBF_4$ or $AgNTf_2$ or AgOAc did not improve the yield of **3a** (entries8-10).

Table 1. Optimization studies[a]



entry	silver salt (20 mol%)	additive (1 equiv)	solvent (2 mL)	NMR yield **3aa** (%)[b]
1	$AgSbF_6$	$AdCO_2H$	DCE	50
2	$AgSbF_6$	$AdCO_2H$	TFE	nd
3	$AgSbF_6$	$AdCO_2H$	THF	45
4	$AgSbF_6$	$AdCO_2H$	dioxane	20
5	$AgSbF_6$	PivOH	DCE	55
6	$AgSbF_6$	AcOH	DCE	44
7	$AgSbF_6$	NaOAc	DCE	nd
8	$AgBF_4$	PivOH	DCE	26
9	$AgNTf_2$	PivOH	DCE	50
10	AgOAc	PivOH	DCE	nd
11[c]	none	PivOH	DCE	37
12[d]	none	PivOH	DCE	traces
13[e]	$AgSbF_6$	PivOH	DCE	75(72)[f]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), Silver salt (20 mol%), additive (1 equiv), Solvent (2 mL), 100 °C for 12 h. [b] ^1H NMR yield (using 1,3,5-trimethoxybenzene as an internal standard). [c] $[RhCp^*(CH_3CN)_3][SbF_6]_2$ was used. [d] $[RhCp^*(OAc)_2]$ was used. [e] 0.4 mmol of **1a** and 0.2 mmol of **1a** were used. [f] Isolated yield. nd = not detected. AcOH= acetic acid, PivOH= pivalic acid.

Changing the catalyst to cationic rhodium complex $[RhCp^*(CH_3CN)_3][SbF_6]_2$ or acetate complex of rhodium $[RhCp^*(OAc)_2]$ was also not useful (entries 11 and 12). Finally, the optimal conditions were achieved by performing the reaction of 0.4 mmol of **1a** with 0.2 mmol of **2a**, using $AgSbF_6$ (20 mol%), and PivOH (1 equiv) in DCE (2 mL) at 100 °C for 12 h, which furnished the product **3aa** in 75% yield (entry 13, and see the SI, Table-SI-4 to 10 for a detailed optimization studies). It is important to note that the excess of unreacted arylacetamide **1a** was recovered successfully.

Having established the optimal reaction conditions for *ortho*-alkenylation of arylacetamides (entry 13, Table 1), the scope of the reaction was explored by employing a variety of arylacetamide derivatives (Scheme 2). Thus, *N*-isopropyl, *N*-*tert*- butyl, *N*-methyl and *N*,*N*-dimethyl groups substituted arylacetamides reacted smoothly with **2a** under the optimal reaction conditions furnishing the products **3aa**, **3ba**, **3ca** and **3da** in 72, 54, 58, and 60% yields, respectively. Arylacetamide derivatives with halogen substitution on the *para*-position of the arylacetamides also underwent a smooth reaction with **2a** yielding the products **3ea-3ha** in moderate yields. 4-Methyl substituted arylacetamide furnished

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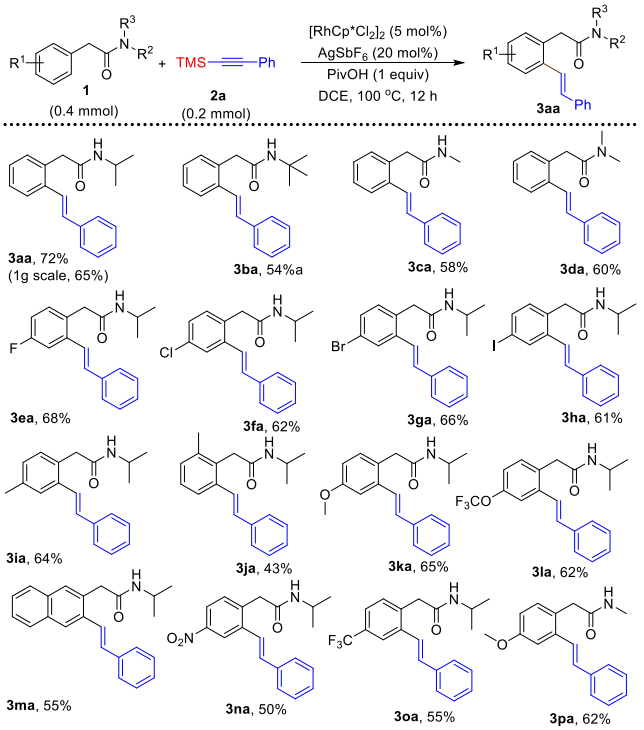
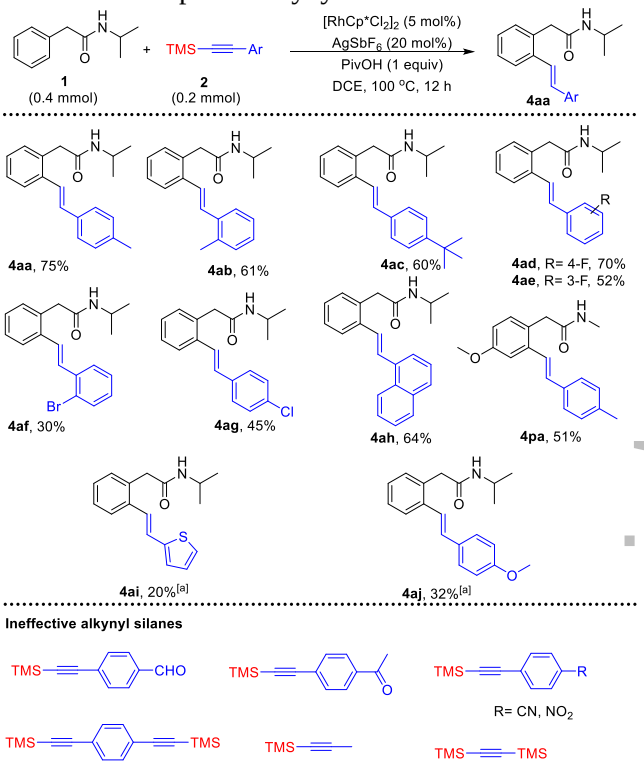
Scheme 2. Substrate scope for arylacetamide derivatives[a,b]



[a] 1 equiv of $AdCO_2H$ was used instead of PivOH.

Scheme 3. Scope for alkynyl silane derivatives



[a] NMR yield.

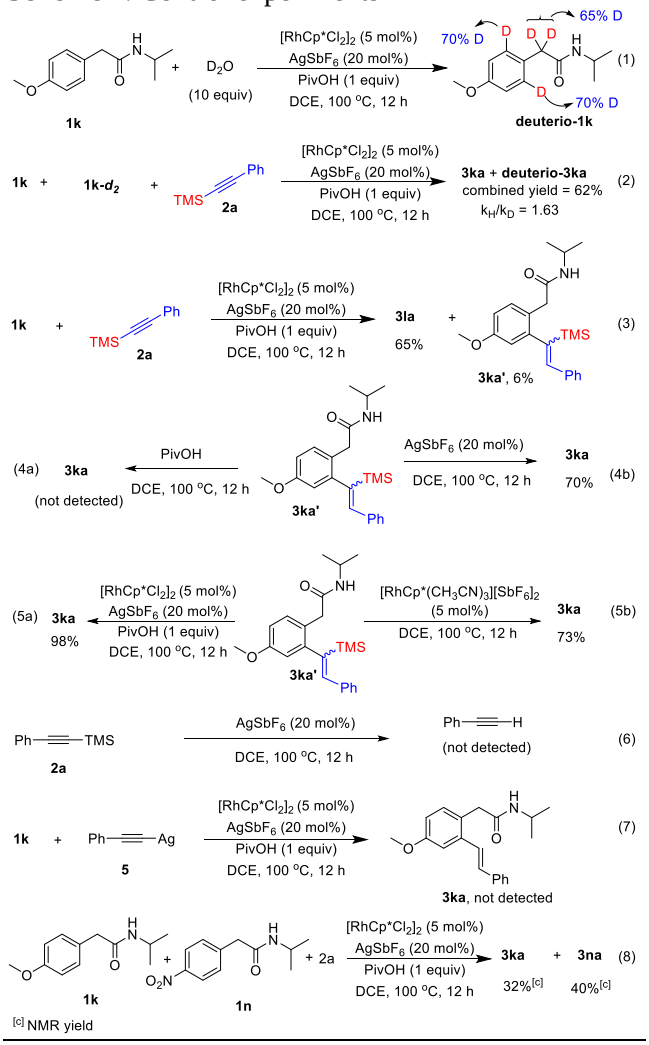
the product **3ia** in 64% yield, whereas 2-methyl substituted arylacetamide afforded the product **3ja** in 43% yield. The low yield of **3ja** could be attributed to the steric crowding exerted by the presence of a methyl group at the *ortho*-position. 4-Methoxy and 4-trifluoromethoxy substituted arylacetamides showed good reactivity with **2a** and rendered the products **3ka** and **3la** in 65 and 62% yields, respectively. The reaction of 2-naphthylacetamide with **2a** furnished the product **3ma** in 55% yield. The substrates with electron-withdrawing groups such as NO_2 and CF_3 on aylacetamides at the *para*-position afforded the products **3na** and **3oa** in 50 and 55% yields, respectively. 2-(4-Methoxyphenyl)-*N*-methylacetamide reacted with **2a** under optimal reaction conditions furnishing the product **3pa** in 62% yield. A scale up experiment of trimethyl(phenylethynyl)silane **2a** (5.74 mmol, 1g) with **1a** afforded the corresponding product **3aa** in 65% isolated yield.

Next, we turned our attention to explore the scope of the reaction with arylalkynylsilane derivatives (Scheme 3). Thus, arylalkynyl silane derivatives with methyl and *tert*-butyl substitution on the various positions of the aryl ring of arylalkynyl silane reacted smoothly with **1a** affording the products **4aa-4ac** in good to moderate yields. The arylalkynyl silane derivatives with halogen substitution on the aryl ring reacted with **1a** furnishing the products **4ad-4ag** in moderate yields. 1-Naphthyl derived alkynyl silane underwent a smooth reaction with **1a** rendering the product **4ah** in 64% yield. Further the reaction of 2 -(4-methoxyphenyl)-*N*-methylacetamide with 4-methyl substituted arylalkynyl silane under the optimal reaction conditions afforded the product **4pa** in 51% yield. The reactions of **1a** with 2-thipophene and 4-anisole derived arylakynyl silane derivatives were less productive affording the corresponding alkenylated products **4ai** and **4aj** in 20 and 32% yields, respectively. Electron-withdrawing group bearing arylalkynyl silane and alkylalkynyl silanes are found to be ineffective under the reaction conditions. Moderate yields obtained in most of the cases are due to the incomplete consumption of alkynylsilane.

To gain insight into the reaction mechanism, a few control experiments were performed (Scheme 4). 4-Methoxy arylacetamide **1k** was reacted with D_2O (10 equiv) under the optimal reaction conditions to obtain 70% deuterium incorporation at the *ortho*- position of the arylacetamide. This reaction indicates that the C-H activation may be a reversible process (Scheme 4, eq 1). The competitive reaction between 4-methoxy arylacetamide **1k** and **1k-*d*$_2$** with **2a** (in the same vessel) furnished a mixture of **3ka** and **deuterio-3ka** in a ratio of 1.63:1 in 62% of yield (Scheme 4, eq 2) suggesting that the C-H activation step may not be involved in the rate determining step. Most importantly, the reaction of **1k** with **2a** under the optimal reaction conditions furnished a non desilylated *ortho*-alkenylated product **3ka'** in 6% yield along with the expected product 3ka in 65% yield (Scheme 4, eq 3). These experiments indicate that **3ka'** could be a possible intermediate in the reaction. Additionally, these experiments reveal that desilylation is taking place after the alkyne insertion

to the metallacycle rather than prior to the alkyne insertion step. It is noteworthy to mention that the silylated product **3ka'** was observed only in the case of aryacetamide **1k**. Whereas, other arylacetamides did not furnish any silylated intermediates, which may be attributed to the concomitant desilylation. Next, we turned our attention to find out the reagent which is responsible for the desilylation. We hypothesized that acid present in the medium could be responsible for desilylation. Therefore, we treated the intermediate **3ka'** with PivOH, which did not furnish the corresponding desilylated product **3ka** (Scheme 4, eq 4a), suggesting that PivOH has no role in the desilylation step. Next, the reaction of **3ka'** with $AgSbF_6$ in DCE at 100 °C for 12 h furnished the corresponding desilylated product **3ka** in 70% yield (Scheme 4, eq 4b). These experiments suggest the probable involvement of $AgSbF_6$ in the desilylation step. However, under the reaction conditions, no $AgSbF_6$ would remain, as 20 mol% of $AgSbF_6$ is required to generate the active Rh-species **A** from $[RhCp^*Cl_2]_2$ (5 mol%). Therefore, the compound **3ka'** was subjected to the standard reaction conditions (which *in situ* forms a cationic species, [RhCp*(OPiv)] $[SbF_6]$, and promotes the desilylation).

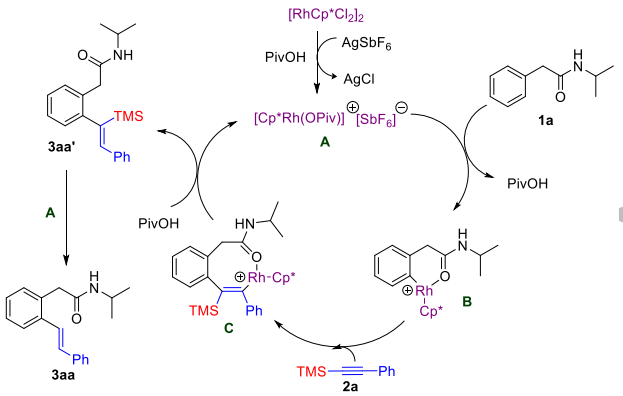
Scheme 4. Control experiments



As expected, this reaction afforded the desilylated product **3ka** in 98% yield (eq 5a). Additionaly, treating the compound **3ka'** with the cationic rhodium complex such as $[RhCp^*(CH_3CN)_3][SbF_6]_2$, also furnished the desilylated product **3ka** in 73% yield (eq 5b). These two experiments (eqs 5a and 5b) indicate that Rh-species **A** is likely to be Lewis acidic, which is responsible for the desilylation. Next, we treated arylalkynyl silane **2a** with $AgSbF_6$, which failed to furnish the phenylacetylene (corresponding desilylated product), suggesting that $AgSbF_6$ can desilylate only the vinylsilane **3ka'** and not an alkynyl silane **2a** (Scheme 4, eq 6). We hypothesized that phenylalkynyl silane **2a** can form silver phenylacetylide **5** in the presence of $AgSbF_6$ and can lead to the corresponding alkenylated product. Therefore, we performed a reaction of **1k** with **5** under the optimal reaction conditions, which failed to furnish the product **3ka**, suggesting that silver phenylacetylide **5** may not be an intermediate in this reaction (Scheme 4, eq 7). As seen in eq 8, a reaction of arylacetamides **1k** and **1n** indicates that the electronic factors may not influence the outcome of the reaction.

Based on the control experiments, our previous work[13d] and literature precedence,[5,6] a plausible mechanism has been proposed (Scheme 5). An *in situ* generated catalytically active species **A** reacts with **1a** forming a 6-membered rhodacycle **B** through a concerted metalation-deprotonation pathway. Insertion of arylalkynyl silane **2a** to the rhodacycle **B** forms an 8-membered intermediate **C**, which undergoes protodemetallation promoted by PivOH forming the corresponding non desilylated alkenylated product **3aa'** and regenerates the active catalyst **A**. Probably, the intermediate **3aa'** undergoes protodesilylation triggered by the complex **A** (Scheme 4, eq 5a,b), forming the corresponding alkenylated product **3aa**.

Scheme 5. Proposed mechanism



In conclusion, we have developed a challenging Rh(III)-catalyzed distal C-H alkenylation reaction using weakly coordinating arylacetamide group under redox-neutral process. To overcome the incompatibility of a terminal alkyne, and its synthetic

equivalents in Rh(III)-catalysis, we successfully utilized arylalkynyl silane as a surrogate. Control experiments suggest that *in situ* generated Rh-species, which is likely to be Lewis acid, plays a vital role in the desilylation step. The methodology offers a broad substrate scope furnishing products in moderate to good yields. The Cp*M-catalyzed distal C-H functionalization of arylacetamide derivatives are less common, and the present result is one of the limited successful examples.

Experimental Section

Procedure for *ortho* alkenylation of arylacetamide derivatives

In a 8-mL screw-cap reaction vial, aryl acetamide derivatives (0.4 mmol), 1-phenyl-2-trimethylsilylacetylene derivatives (0.2 mmol), rhodium catalyst $[RhCp^*Cl_2]_2$ (6.2 mg, 5 mol%), PivOH (20.4 mg, 1 equiv), $AgSbF_6$ (13.7 mg, 20 mol%) in DCE (2 mL) were taken. The vial was sealed with a screw cap and placed in a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using EtOAc/ petroleum ether mixture or EtOAc/DCM mixture.

Acknowledgements

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