

Rhodium-Catalyzed Cross-Coupling of Vinylarenes with Arylaluminum Reagents in the Presence of Ketones

Shota Tanaka^[a] and Atsunori Mori*^[a]

Keywords: Rhodium / Aluminum / Addition / Elimination / Cross-coupling

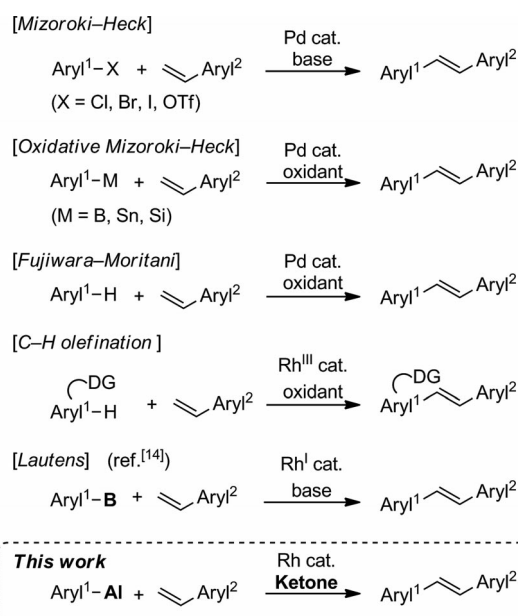
Rhodium-catalyzed addition/elimination of arylaluminum reagents with vinylarenes was achieved to obtain stilbene derivatives. The reaction of diethyl(phenyl)aluminum with styrene in the presence of the chloro(1,5-cyclooctadiene)rhodium(I) dimer, [RhCl(cod)]₂, and diisopropyl ketone (2,4-dimethyl-3-pentanone) as an additive occurred to give (*E*)-stil-

bene in quantitative yield. The use of other arylaluminum reagents afforded β-arylated products in good to excellent yields. This reaction was found to be promoted by ketones as additives, which are reduced to the corresponding alcohols, as confirmed by analysis of the crude reaction mixture by ¹H NMR spectroscopy.

Introduction

Organoaluminum reagents have played a significant role in organic chemistry as Lewis acids, nucleophiles and cocatalysts for olefin polymerization.^[1] In particular, C–C bond-formation reactions with organoaluminum reagents such as 1,2-addition to carbonyl compounds,^[2] conjugate addition to enones,^[3] and cross-coupling with organic halides^[4] are known, and these reagents have been widely used in organic synthesis as nucleophiles that are more functional-group-tolerant than organomagnesium and organolithium reagents. The development of novel reactions with organoaluminum reagents is thereby an important issue in organic synthesis. Although a number of C–C bond-formation reactions with organoaluminum species have been developed, addition/elimination-type reactions with olefins have to the best of our knowledge not been reported. Accordingly, we envisaged that it would be intriguing to develop an addition/elimination-type reaction of arylaluminum reagents with vinylarenes to afford stilbene derivatives, which have attracted much attention as π-conjugated organic materials. The synthesis of stilbene derivatives by using addition/elimination can be categorized as summarized in Scheme 1. The palladium-catalyzed reaction of aryl halides with vinylarenes is well known as the Mizoroki–Heck reaction,^[5,6] and it has been widely used to synthesize biologically active molecules^[7] and various π-conjugated materials^[8] bearing an olefinic moiety. The reactions of main-group organometallic species (boron, silicon, and tin) with vinylic compounds have also been shown to proceed with palladium catalysts

in the presence of an oxidant to afford stilbene, which are recognized as oxidative Mizoroki–Heck-type reactions.^[9] Oxidative C–H coupling of arenes with vinylarenes was also shown to take place with a palladium(II) catalyst (Fujiwara–Moritani reaction),^[10] and a related addition/elimination reaction was recently reported with Cp*Rh^{III} (Cp* = C₅Me₅) complexes at C–H bonds, although the reaction requires the substrate to possess a neighboring directing group (DG).^[11] However, cross-coupling reactions of several main-group arylmetal species bearing no directing group with olefinic compounds catalyzed by a rhodium(I) complex has also attracted much attention.^[12] We have



Scheme 1. Transition-metal-catalyzed cross-coupling of aryl halide or arylmetal species with vinylarenes. Tf = trifluoromethylsulfonfyl.

[a] Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan
E-mail: amori@kobe-u.ac.jp
http://www2.kobe-u.ac.jp/~amori/home/index.html

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.201301757>.

shown that several main-group reagents such as boron, silicon, and tin react with α,β -unsaturated carbonyl compounds;^[13] however, few reactions have been shown to proceed with a simple olefin. Pioneering work on rhodium(I)-catalyzed addition/elimination reactions of arylboronic acids to styrene was reported by Lautens and co-workers.^[14] Herein, we report that arylaluminum reagents effectively react with vinylarenes in the presence of a rhodium(I) catalyst to undergo Mizoroki–Heck-type addition/elimination reactions, in which the ketone as an additive plays a key role in the catalytic reaction.

Results and Discussion

We first investigated the rhodium-catalyzed reaction of diethyl(phenyl)aluminum (**1a**) with styrene (**2a**). Preparation of **1a** was performed with diethylaluminum chloride and phenylmagnesium bromide.^[15] As summarized in Table 1, the reaction of **1a** with **2a** in the presence of $[\text{RhCl}(\text{cod})]_2$ (2.5 mol-%; cod = 1,5-cyclooctadiene) at 60 °C for 3 h took place to afford (*E*)-stilbene (**3aa**) in 43% yield. Increasing the reaction time to 24 h did not improve the yield (Table 1, Entry 2). Increasing the loading of $[\text{RhCl}(\text{cod})]_2$ (5.0 mol-%) slightly improved the yield of **3aa** to 61% (Table 1, Entry 3). By contrast, if 2.0 equiv. of diisopropyl ketone was employed as an additive, the reaction proceeded smoothly to give **3aa** in quantitative yield (Table 1, Entry 4). The reaction of **1a** with **2a** performed at room temperature also proceeded, but the yield was slightly lower (56%; Table 1, Entry 5). The use of toluene as a solvent also gave **3aa** in quantitative yield at 60 °C after 3 h (Table 1, Entry 6). The reaction also proceeded with the use of acetone or pinacolone (3,3-dimethyl-2-butanone) as an additive instead of diisopropyl ketone (Table 1, Entries 7 and 8). By using $[\text{Rh}(\text{OH})(\text{cod})]_2$, **3aa** was delivered in excellent yield (93%). $[\text{Rh}(\text{OMe})(\text{cod})]_2$ also served as an effective catalyst to afford **3aa** in 62% yield, whereas $[\text{RhCl}(\text{nbd})]_2$ (nbd = norbornadiene) and Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$, were ineffective in this reaction. Upon using $[\text{RhCp}^*\text{Cl}_2]_2$ as the catalyst, the reaction did not occur at all (Table 1, Entry 13). The reaction of dimethyl(phenyl)aluminum with styrene in the presence of $[\text{RhCl}(\text{cod})]_2$ took place to give **3aa** in quantitative yield (Table 1, Entry 14). Although the reaction of phenylaluminum dichloride occurred, the yield of **3aa** was lower (38%; Table 1, Entry 15). In contrast with our previous reports, in which only hydroxy- and methoxyrhodium complexes were effective in Mizoroki–Heck-type addition/elimination reactions of α,β -unsaturated carbonyl compounds and in which chlororhodium complexes showed little efficiency, the use of chlororhodium complexes effectively induced the catalytic reaction with arylaluminum reagents.

We next performed the rhodium-catalyzed reaction of several arylaluminum reagents with various vinylarenes **2**. The results are summarized in Scheme 2. The reaction of **1a** with 4-methylstyrene (**2b**) and 4-methoxystyrene (**2c**) at 60 °C for 3 h proceeded to give β -phenylated products **3ab**

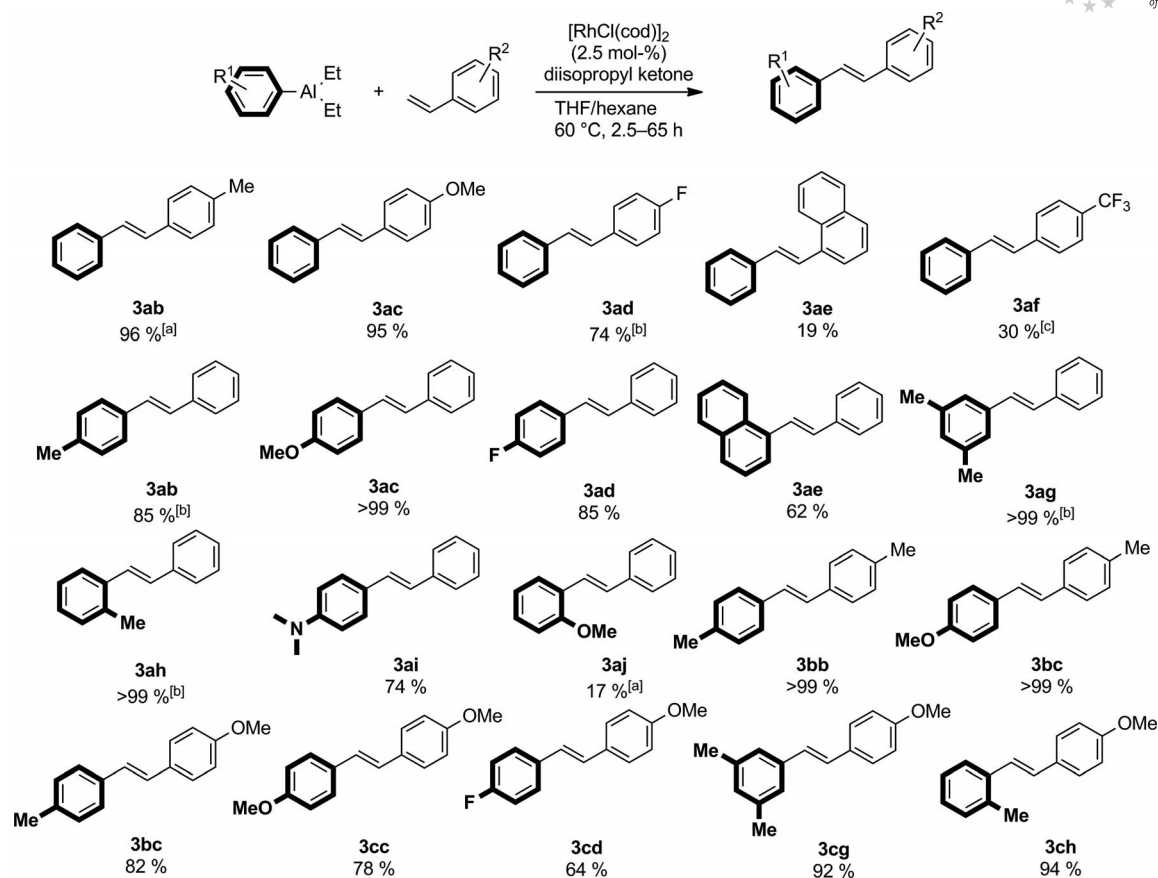
Table 1. Reaction of a phenylaluminum reagent with styrene catalyzed by a rhodium complex.^[a]

Entry	R	Catalyst (mol-%)	Additive	Yield ^[b] [%]
1	Et	$[\text{RhCl}(\text{cod})]_2$ (2.5)	none	43
2 ^[c]	Et	$[\text{RhCl}(\text{cod})]_2$ (2.5)	none	45
3	Et	$[\text{RhCl}(\text{cod})]_2$ (5.0)	none	61
4	Et	$[\text{RhCl}(\text{cod})]_2$ (2.5)	diisopropyl ketone	>99
5 ^[d]	Et	$[\text{RhCl}(\text{cod})]_2$ (5.0)	diisopropyl ketone	56
6 ^[e]	Et	$[\text{RhCl}(\text{cod})]_2$ (5.0)	diisopropyl ketone	>99
7	Et	$[\text{RhCl}(\text{cod})]_2$ (2.5)	acetone	72
8	Et	$[\text{RhCl}(\text{cod})]_2$ (2.5)	pinacolone	>99
9	Et	$[\text{Rh}(\text{OH})(\text{cod})]_2$ (2.5)	diisopropyl ketone	93
10	Et	$[\text{Rh}(\text{OMe})(\text{cod})]_2$ (2.5)	diisopropyl ketone	62
11	Et	$[\text{RhCl}(\text{nbd})]_2$ (5.0)	diisopropyl ketone	3 ^[f]
12	Et	$[\text{RhCl}(\text{PPh}_3)_3]$ (5.0)	diisopropyl ketone	3 ^[f]
13	Et	$[\text{RhCp}^*\text{Cl}_2]_2$ (2.5)	diisopropyl ketone	0
14	Me	$[\text{RhCl}(\text{cod})]_2$ (2.5)	diisopropyl ketone	>99
15 ^[g]	Cl	$[\text{RhCl}(\text{cod})]_2$ (2.5)	diisopropyl ketone	38

[a] Unless otherwise noted, the reaction was performed with styrene (0.5 mmol), arylaluminum reagent (1.0 mmol), and additive (1.0 mmol) in THF (1.0 mL) and hexane (1.0 mL) at 60 °C for 3 h. [b] Yield of isolated product. [c] The reaction time was 24 h. [d] The reaction was performed at room temperature. [e] Toluene was used as the solvent. [f] The yield was determined by analysis of the reaction mixture by ¹H NMR spectroscopy. [g] The reaction time was 20 h.

and **3ac** in 96% and 95% yield, respectively. The reaction of 4-fluorostyrene (**2d**) also took place to give **3ad** in good yield (74%). Although the reaction of more bulky 1-vinylnaphthalene (**2e**) occurred, the yield of **3ae** was decreased to 19%. The reaction of electron-deficient 4-(trifluoromethyl)styrene (**2f**) with **1a** proceeded to afford **3af** in 30% yield. The reaction of various styrene derivatives with other arylaluminum reagents, that is, 4-methylphenyl-, 4-methoxyphenyl-, 4-fluorophenyl-, 3,5-dimethylphenyl-, 2-methoxyphenyl-, 1-naphthyl-, and 4-(dimethylamino)phenylaluminum, occurred to afford the β -arylated products in good to excellent yields. The reaction of diethyl(2-methoxyphenyl)aluminum delivered the product in poor yield, which might be the result of poisoning by a coordinating methoxy substituent, whereas the related noncoordinating methyl substituent gave **3ah**, and distal methoxy and dimethylamino groups (leading to **3ai** and **3bc**) did not decrease the yield.

We then performed the reaction of other arylmetal species with styrene (**2a**). These results are summarized in Table 2. The reaction of aryllithium species with styrene in the presence of a rhodium catalyst did not afford desired product **3ba** (Table 2, Entry 1). The reaction of arylmagnesium bromide with **2a** gave **3ba** in only 9% yield. In contrast with the reaction of arylaluminum species, the use of diisopropyl ketone as an additive for the Grignard reagent was ineffective (Table 2, Entry 3). The reaction of arylzinc chloride, which was obtained from the aryl Grignard reagent and $\text{ZnCl}_2 \cdot (\text{tmeda})$ complex (tmeda = *N,N,N',N'*-



Scheme 2. Reaction of arylaluminum reagents with vinylarenes. The reaction was performed with **1a** (1.0 mmol), vinylarene (0.5 mmol), diisopropyl ketone (1.0 mmol), and $[\text{RhCl}(\text{cod})_2]$ (0.0125 mmol) in THF (2.0 mL) and hexane at 60 °C for 2.5–65 h. The yield of the isolated product was determined. [a] The yield was estimated by analysis of the reaction mixture by ^1H NMR spectroscopy. [b] The yield was estimated by analysis of the reaction mixture by GC. [c] The reaction was performed with styrene **2f** (0.3 mmol).

tetramethylethylenediamine), with **2a** took place; however, **3ba** was afforded in a low 49% yield (Table 2, Entry 4). The addition of a ketone to the reaction of an arylzinc reagent with styrene gave **3ba** in a slightly higher yield (59%; Table 2, Entry 5). The use of a triarylaluminum species as a nucleophile also proceeded to give product **3ba** in a lower yield (42%; Table 2, Entry 6). The reaction of an aluminum ate complex, that is, $\text{Ar-Al}(i\text{Bu})_3\cdot\text{MgBr}$, which was prepared from the aryl Grignard reagent and triisobutylaluminum, proceeded to give the product in 48% yield (Table 2, Entry 7). Phenylboronic acid and trimethoxy(phenyl)silane also reacted with styrene in toluene at 100 °C to afford the corresponding stilbenes in 35 and 41% yield, respectively (Table 2, Entries 8 and 9). These results suggest that reactions with stronger nucleophiles, including magnesium and lithium reagents, induce direct nucleophilic attack at the ketone, whereas insufficient reduction may result in inferior yields with zinc, boron, and silane reagents.

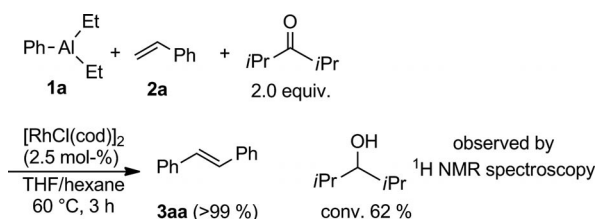
The effect of the ketone in this addition/elimination reaction was investigated, as shown in Scheme 3. The reaction of **1a** with **2a** was performed at 60 °C for 3 h in the presence of diisopropyl ketone or pinacolone to observe the corresponding secondary alcohol by analysis of the crude reaction mixture by ^1H NMR spectroscopy (see also the Sup-

Table 2. Reaction of various arylmetal species with styrene.^[a]

Entry	Aryl-M	Additive	Time [h]	Yield ^[b] [%]
1 ^[c,d]	<i>p</i> TolLi	none	4	0
2	<i>p</i> TolMgBr	none	3	9 ^[e]
3	<i>p</i> TolMgBr	diisopropyl ketone	3	11 ^[e]
4	<i>p</i> TolZnCl·(tmeda)	none	17	49
5	<i>p</i> TolZnCl·(tmeda)	diisopropyl ketone	14	59
6	(<i>p</i> Tol) ₃ Al	diisopropyl ketone	14	42
7 ^[d]	<i>p</i> TolAl <i>i</i> Bu ₃ ·MgBr	diisopropyl ketone	18	48
8 ^[f]	PhB(OH) ₂	diisopropyl ketone	13	35
9 ^[f]	PhSi(OMe) ₃	diisopropyl ketone, TBAF ^[g]	13	41

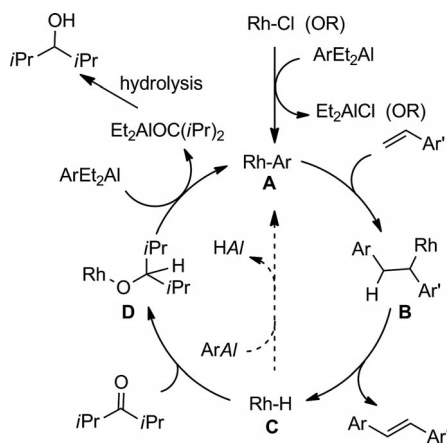
[a] Unless otherwise noted, the reaction was performed with the arylmetal species (0.6 mmol), styrene (0.3 mmol), $[\text{RhCl}(\text{cod})_2]$ (0.015 mmol), and the additive (0.6 mmol) in THF (1.2–2.8 mL) at 60 °C. [b] Yield of isolated product. [c] The reaction was performed in toluene at room temperature. [d] The reaction was performed with **2a** (0.5 mmol). [e] The yield was estimated by analysis of the reaction mixture by ^1H NMR spectroscopy. [f] The reaction was performed with $[\text{Rh}(\text{OH})(\text{cod})_2]$ (5.0 mol-%) at 100 °C in toluene. [g] TBAF = tetrabutylammonium fluoride.

porting Information), which showed that reduction of the ketone occurred in the catalytic system.



Scheme 3. Studies on the effect of ketone in the reaction of an arylaluminum reagents with vinylarene.

On the basis of the above experiments a plausible reaction mechanism is shown in Scheme 4. Transmetalation of the aryl group in the arylaluminum species to rhodium chloride as well as to the hydroxy and alkoxy complexes occurs to afford arylrhodium species **A**. Insertion of styrene into the carbon–metal bond of **A** forms **B**, which undergoes β -hydride elimination to give stilbene along with hydridorhodium species **C**. Obtained complex **C** reacts with the ketone to give rhodium alkoxide complex **D**, which is capable of inducing transmetalation with the arylaluminum species to regenerate arylrhodium complex **A** and the corresponding aluminum alkoxide. This aluminum alkoxide is transformed into the alcohol by hydrolysis after quenching the reaction mixture.^[16] Hydridorhodium compound **C** may also undergo transmetalation with the arylmetal species to give zinc and **A**, which thereby results in a less efficient catalytic reaction in the absence of the ketone with neutral aluminum (see Table 1, Entries 1–3 and Table 2, Entry 4); however, the formation of the rhodium alkoxide by reduction of the ketone would facilitate transmetalation, which results in a highly efficient catalytic reaction.



Scheme 4. Plausible mechanism for the catalytic addition/elimination reaction of arylaluminum reagents with vinylarenes.

Conclusions

A rhodium-catalyzed cross-coupling reaction of arylaluminum reagents with vinylarenes was shown to take place. The use of a ketone as an additive, which behaves as a hy-

dride acceptor of the rhodium species, drastically promoted the catalytic reaction. Although such a rhodium-catalyzed addition/elimination reaction has only been shown to proceed with α,β -carbonyl compounds with main-group reagents, that is, boron, silicon, and tin, we have shown that a more organometallic aluminum species can also be an available reagent, with which the scope of the reaction is enlarged.

Experimental Section

General: All the reactions were performed under nitrogen. ¹H (300 MHz) and ¹³C NMR (75 MHz) spectra were measured with a Varian Gemini 300 as CDCl₃ solutions unless noted. The chemical shifts are expressed in ppm with CHCl₃ (δ = 7.26 ppm for ¹H) or CDCl₃ (δ = 77.0 ppm for ¹³C) as internal standards. High-resolution mass spectra (HRMS) were measured with a JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254) were used. Purification by HPLC with a preparative SEC column (JAI-GEL-2 H) was performed by JAI LC-9201. Gas chromatography analyses were performed with a Shimadzu GC-MS-QP2010 Plus. The arylmagnesium bromides were prepared from the aryl bromides and magnesium turnings. The rhodium catalysts [RhCl(cod)]₂,^[17] [Rh(OH)(cod)]₂,^[18] [Rh(OMe)(cod)]₂,^[18] and [RhCp*Cl₂]₂^[19] were prepared according to literature procedures. ZnCl₂(tmeda) was prepared according to a literature procedure.^[20] The ketones (diisopropyl ketone, acetone, and pinacolone) were dried with molecular sieves (3 Å) and stored overnight prior to use. For the solvent of the rhodium-catalyzed reactions, anhydrous THF and toluene were employed. Other chemicals were purchased and used without further purification.

General Procedure for the Reaction of Arylaluminum Reagents with Vinylarenes: A 20 mL Schlenk tube equipped with a magnetic stirring bar was charged with diethylaluminum chloride (1.05 M in hexane, 1.0 mmol, 0.95 mL). Then, a solution of arylmagnesium bromide (1.0 M in THF, 1.0 mmol, 1.0 mL) was slowly added dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. Styrene (0.5 mmol, 0.057 mL), diisopropyl ketone (1.0 mmol, 0.142 mL), and [RhCl(cod)]₂ (0.0125 mmol, 6.1 mg) were added to the resulting white suspension, and the mixture was stirred at 60 °C for 2.5–65 h. After cooling to room temperature the reaction mixture was quenched with water (**CAUTION:** Gas evolution occurs!). 1.0 M HCl (1.0 mL) was then added, and the solution was poured into a mixture of diethyl ether/water, which resulted in the separation of two phases. The aqueous phase was extracted with diethyl ether (2×), and the combined organic layers were dried with anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel and preparative SEC.

Supporting Information (see footnote on the first page of this article): Experimental details and characterization of new compounds.

Acknowledgments

This work was supported by Kakenhi B (No. 25288049) and the Japan Society for the Promotion of Science (JSPS). S. T. thanks JSPS for a Research Fellowship for Young Scientists.

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Received: November 22, 2013
Published Online: January 17, 2014