tallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-100685. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] Examples of trigonally coordinated Li: a) M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, R. Shakir, *J. Am. Chem. Soc.* **1983**, *105*, 302–304; b) L. M. Engelhardt, B. S. Jolly, P. C. Punk, C. L. Raston, B. W. Skeleton, A. H. White, *Aust. J. Chem.* **1986**, *39*, 133; c) P. G. Willard, M. A. Nichols, *J. Am. Chem. Soc.* **1991**, *113*, 9671–9673; d) H. Görls, B. Neumüller, A. Scholz, J. Scholz, *Angew. Chem.* **1995**, *107*, 732–735; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 673–676.

[9] The negative charge of the aminopyridinato ligand is not localized on the amido nitrogen atom.

[10] Compound **5** is not accessible by transmetalation with YCl_3 and three equivalents "TMS-ApLi" (ether/pyridine); this procedure affords compound **1** instead.

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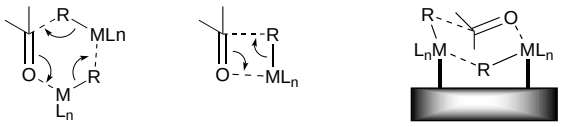
[12] Sincere thanks are due to the referee who provided this information.

Rate Acceleration in Nucleophilic Alkylation of Carbonyl Compounds with a New Template Containing Two Metallic Centers**

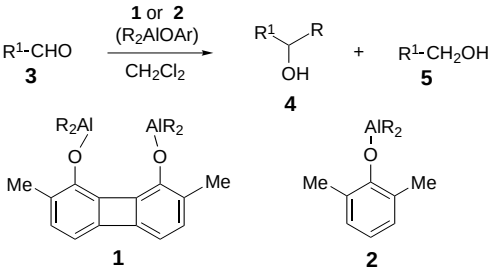
Takashi Ooi, Makoto Takahashi, and Keiji Maruoka*

The nucleophilic addition of reactive organometallic reagents to carbonyl compounds is undoubtedly one of the most thoroughly investigated of all organic transformations because of sustained interest in its mechanism and selectivity, as well as numerous applications to a variety of syntheses in the fields of natural products, pharmacology, and material science.[1]

The preferred transition state for addition of Grignard and organoaluminum reagents is often a cyclic six-membered array (**A**) that contains a carbonyl group and two molecules of organometallic reagent.[2] With the same reactants in a 1:1 ratio, a four-centered transition state (**B**) is also conceivable, although alkylation proceeds more slowly by this route. Hence, facilitation of the six-membered transition state **A** is



crucial in order to achieve high reactivity, particularly in the case of less reactive organometallic reagents. In this context, we became interested in designing new molecules of type **C** with two metallic centers that would permit simple alkylation of carbonyl compounds with otherwise less reactive alkylmetal species.[3] Here we report initial results with the modified bis(dialkylaluminum) reagent **1**, an efficient alkyl-transfer system for aldehydes (Scheme 1).[4]



Scheme 1. Alkylation of aldehydes with dialkylaluminum reagents.

Treatment of benzaldehyde (**3**; $R^1 = Ph$) with one equivalent of Me_3Al in CH_2Cl_2 at $-78\,^\circ C$ gave a long-lived monomeric 1:1 complex that gradually decomposed to 1-phenylethanol (**4**; $R^1 = Ph$, $R = Me$) on warming to $-20\,^\circ C$.[5] Use of (2,6-dimethoxyphenyloxy)dimethylaluminum (**2**, $R_2 = Me$) instead of Me_3Al significantly retarded the rate of alkylation under similar reaction conditions. Even use of excess **2** (2 equiv) failed to yield methylation product **4** at $-20\,^\circ C$. In marked contrast, however, methylation of benzaldehyde proceeded quite smoothly with one equivalent of 2,7-dimethyl-1,8-biphenylenedioxybis(dimethylaluminum) (**1**; $R = Me$) at $-20\,^\circ C$ to furnish after 4 h 1-phenylethanol (**4**; $R^1 = Ph$, $R = Me$) in 84% yield.[6] With higher alkyl derivatives of **1** ($R = Et$, Hex), alkylation was accompanied by concomitant formation of reduction product **5**, and different aldehydes gave equally good results (Table 1).

Table 1. Alkylation of aldehyde **3** with dialkylaluminum reagents.[a]

Entry	R^1	R	Reaction conditions [°C, h][a]	Yield of **4** and **5** [%][b] Use of **1**	Use of **2**
1	Ph	Me	−20,4	84	0
2	Ph	Et	−78,1; −40,2	71 (11)	10 (2)
3	Ph	Hex	−78,1; −40,1.5	60 (36)	6 (5)
4	*c*Hex	Me	−78,1; −40,3; −20,3	63	4[c]
5	*c*Hex	Et	−78,2; −40,3	52 (22)	10 (9)
6	*c*Hex	Et	−78,2; −40,3[d]	50 (20)	3 (2)
7	C_9H_{19}	Me	−20,4.5	86	< 1

[a] Alkylation was carried out under the reaction conditions cited with **1** (1 equiv) or **2** (2 equiv) in CH_2Cl_2. [b] Yield of **5** in parentheses. [c] Aldol product through self-condensation. [d] Use of dilute CH_2Cl_2 solution.[7]

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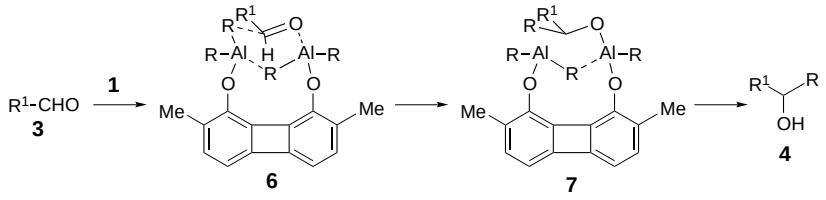
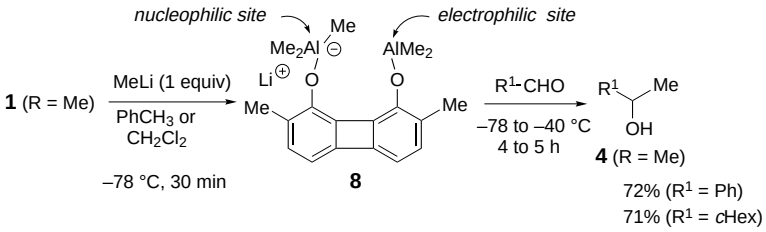
The observed rate acceleration is readily understandable in terms of the mechanism outlined in Scheme 2. Upon reaction of **1** with aldehyde **3**, the 1:1 coordination complex **6** is initially



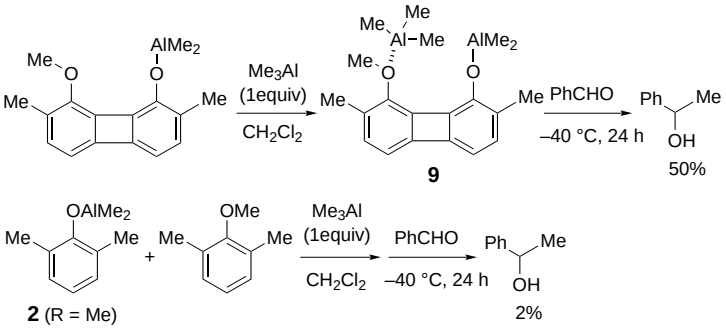
Scheme 2. Plausible mechanism for rapid alkylation of aldehydes with **1**.

formed, which is easily transformed by way of a cyclic six-membered transition state into alkylation product **7**.[6] Formation of the persistent alkoxyaluminum bond in **7** requires use of a stoichiometric amount of **1** for nucleophilic carbonyl alkylation. The formation of reduction product **5** as a by-product from bis(dialkylaluminum) reagent **1** when R = ethyl or hexyl is assumed to be a result of β-hydride transfer from the alkyl residue.

Our hypothesis is further supported by alkylation experiments with a modified system that also contains two metallic centers. Thus, initial treatment of bis(dimethylaluminum) derivative **1** (R = Me) with one equivalent of MeLi generates a new amphiphilic alkylation system **8** that possesses both an electrophilic and a nucleophilic center (Scheme 3). This compound proved to be much more effective than the



Scheme 3. Alkylation by way of the methyllithium adduct **9**.



Scheme 4. Methylation of benzaldehyde after coordination of Me_3Al with a methyl ether.

symmetric compound **1**, and carbonyl alkylation of aldehyde **3** with **8** proceeds even at temperatures between −78 and −40 °C (see entry 1 of Table 1). However, similar alkylations with monoaluminum derivative **2** (R = Me) and its complex with MeLi produced only traces of **4** (R = Ph; < 3% yield). This indicates that appropriate placement of the two metallic centers is essential for achieving the remarkable rate enhancement in the new amphiphilic alkylation.

To supply proof for the key element in the present suggestion we also prepared another system with two metallic centers (**9**, Scheme 4) on the assumption that proximity provided by coordination of the methyl ether to trimethylaluminum could still confer a certain degree of acceleration in carbonyl alkylation. Indeed, methylation of benzaldehyde with **9** proceeded smoothly at −40 °C to give 1-phenylethanol in 50% yield, whereas a simple combination of the monoaluminum species **2** (R = Me) and 2,6-dimethylanisole dramatically lowered the yield of methylation product under similar reaction conditions.

More appropriate choice of metals and a more sophisticated design for templates are the subjects of ongoing study.

Experimental Section

Alkylation of benzaldehyde (**3**; R^1 = Ph) with **1** (R = Me): A suspension of 2,7-dimethyl-1,8-biphenylenediol (106 mg, 0.5 mmol) in dry CH_2Cl_2 (5 mL) was carefully degassed, and a 2 M solution of Me_3Al in hexane (0.5 μL, 1 mmol) was added at room temperature under argon. The red solution was stirred for 30 min. After cooling to −78 °C, benzaldehyde (51 mL, 0.5 mmol) was added dropwise. The solution was allowed to warm to −20 °C, and stirring was continued for 4 h. The mixture was then poured into ice-cooled 1 N HCl and extracted with ether. The combined ethereal extracts were dried over Na_2SO_4. Evaporation of solvents and purification of the residual oil by column chromatography (silica gel, dichloromethane) gave 1-phenylethanol (**4**, R^1 = Ph, R = Me; 52 mg, 0.43 mmol) as a colorless oil (84% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 7.26–7.40 (5H, m, Ph), 4.91 (1H, dq, J = 3.6, 6.3 Hz, CH), 1.79 (1H, d, J = 3.6 Hz, OH), 1.51 (3H, d, J = 6.3 Hz, CH_3).

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[6] In the initial stages of the reaction, aldehyde **3** forms a chelation complex with **1** as a bidentate Lewis acid, which would be in equilibrium with another complex (**6**) in which the free electron pairs

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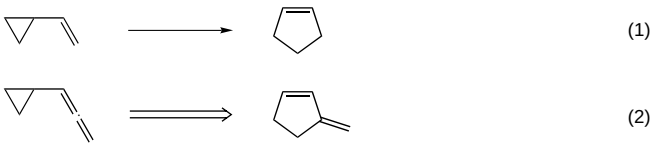
of the carbonyl groups and the alkylaluminum substituents are involved in the coordination. In a chelation complex, alkyl groups R are far removed from the carbonyl center due to the sp^3-like conformation of aluminum, so transfer of an R group from aluminum to the carbonyl center through an unfavorable four-membered transition state seems quite unlikely. See: T. Ooi, M. Takahashi, K. Maruoka, *J. Am. Chem. Soc.* **1996**, *118*, 11307; T. Ooi, E. Tayama, M. Takahashi, K. Maruoka, *Tetrahedron Lett.* **1997**, *38*, 7403. Other examples of bidentate Lewis acids: V. Sharma, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1992**, *114*, 7931; M. Reilly, T. Oh, *Tetrahedron Lett.* **1995**, *36*, 217; *ibid.* **1995**, *36*, 221.

[7] If the proposed mechanism is truly operative, it must be assumed that dilution would not affect the rate of alkylation with **1**, but would further retard reaction with **2**.

Rhodium(I)-Catalyzed Regioselective Ring-Expanding Rearrangement of Allenylcyclopropanes into Methylenecyclopentenes**

Minoru Hayashi, Tadashi Ohmatsu, Yun-Ping Meng, and Kazuhiko Saigo*

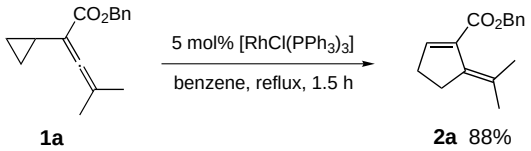
The vinylcyclopropane–cyclopentene rearrangement has attracted much attention owing to its potential synthetic utility.[1–3] The skeletal similarity between vinylcyclopropanes and allenylcyclopropanes led us to examine the rearrangement of allenylcyclopropanes into methylenecyclopentenes; the selective transformation has not yet been reported (Scheme 1).[3–5] Here we describe the first examples of the



Scheme 1. Similarity of the skeletal structures of vinylcyclopropanes and allenylcyclopropanes.

transition metal catalyzed selective transformation of allenylcyclopropanes into methylenecyclopentenes.

Our test of the hypothesis started with the allenylcyclopropane **1a**, which was easily prepared by palladium-catalyzed carbonylation of the benzyl carbonate of 2-methyl-4-cyclopropyl-3-butyn-2-ol. Heating allenylcyclopropane **1a** in refluxing benzene for 1.5 h in the presence of 5 mol% of $[RhCl(PPh_3)_3]$ gave the corresponding methylenecyclopentene **2a** in 88% yield (Scheme 2).



Scheme 2. Rhodium(I)-catalyzed rearrangement of cyclopropylallene **1a**.

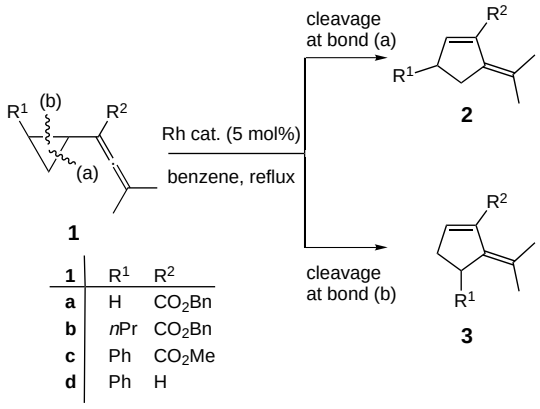
Wender and co-workers reported that a cationic rhodium(I) complex catalyzes the [5+2] cycloaddition of vinylcyclopropanes with alkynes faster than a neutral rhodium complex.[6] However, in our case, the cationic rhodium complex $[Rh(cod)_2]^+BF_4^-$ (cod = 1,5-cyclooctadiene) required a longer reaction time than $[RhCl(PPh_3)_3]$ to complete the rearrangement, although the initial reaction rate was faster (Table 1, entries 1 and 2). These reactions are the first examples of the selective rearrangement of an allenylcyclopropane into the corresponding methylenecyclopentene.

Table 1. Rhodium(I)-catalyzed rearrangement of allenylcyclopropanes

Entry	1	Cat.[a]	t [h]	Products[b]	Yield [%][c]	2:3[d]
1	**1a**	A	1.5	**2a**	88	–
2	**1a**	B	3	**2a**	88	–
3	**1b**	A	1	**2b/3b**	89	88:12
4	**1b**	C	3	**2b/3b**	98	>99:1
5	**1b**	B	10	**2b/3b**	89	>99:1
6	**1c**	A	3	**2c/3c**	99	69:31
7	**1c**	C	0.8	**2c/3c**	98	92:8
8	**1c**	B	14	**2c/3c**	95	5:95
9	**1d**	A	12	**2d/3d**	73	56:44
10	**1d**	D	12	**2d/3d**	79	15:85
11	**1d**	B	12	**2d/3d**	78	3:97

[a] Catalyst A: $[RhCl(PPh_3)_3]$, B: $[Rh(cod)_2]^+BF_4^-$, C: $[Rh(PPh_3)_3]^+BF_4^-$ (prepared in situ from an equimolar mixture of $[RhCl(PPh_3)_3]$ and $AgBF_4$), D: $[Rh(cod)(PPh_3)_2]^+BF_4^-$. [b] Satisfactory analytical and spectral data were obtained for all products listed here. [c] Yield of isolated product. [d] The isomer ratio was determined by ^1H NMR spectroscopy.

When the cyclopropane ring of the allenylcyclopropane bears a substituent, two isomers can be obtained on rearrangement, since there are two possibilities for carbon–carbon bond cleavage. Bond cleavage (a) gives methylenecyclopentene **2**, and cleavage (b) leads to the other regioisomer **3** (Scheme 3).



Scheme 3. Possible ring-opening reactions of the cyclopropane.

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