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REGIOCONTROLLED SYNTHESIS OF ALLYLSILANES BY MEANS OF RHODIUM(I) OR IRIDIUM(I) CATALYZED ISOMERIZATION OF OLEFINS

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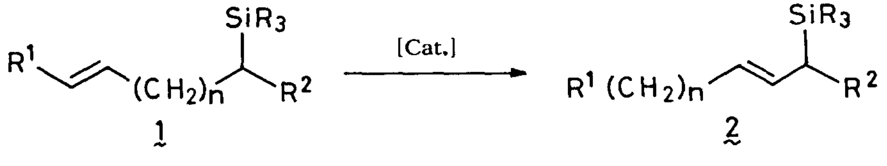
Summary: Rhodium(I) or iridium(I) catalyzed migration of double-bond has been successfully applied to the regiocontrolled synthesis of allylsilane from olefin silylated at a remote sp^3 carbon.

Double-bond migration in olefins is one of the simplest and the most thoroughly studied catalytic reactions.[1, 2] However, it is difficult to obtain the devised single product because the product distribution reflects directly the thermodynamic stability of each compound. Successful examples are limited to the cases having a significant energy difference between starting materials and products.[3] Therefore, the introduction of a pertinent auxiliary as a control factor could provide an indirect method in order to terminate the double-bond migration at the specific site of the molecule. Trimethylsilyl group should be a promising candidate as the auxiliary because of the bulkiness and the proton equivalent character.

On the other hand, allylsilanes emerged as valuable tools in organic synthesis. The regiospecific mode of those is now well-documented in the reaction with a variety of electrophiles.[4] Although a number of methods have been reported for introducing this functionality into a molecule, the problem of the regio- and stereocontrol in the synthesis of **2** has remained largely unsolved. Since only limited examples of the regiocontrol have been reported,[5] an unambiguous and facile approach is desirable. Thus, we describe here a regiocontrolled synthesis of **2** by means of rhodium(I) or iridium(I) catalyzed isomerization of olefin **1**.

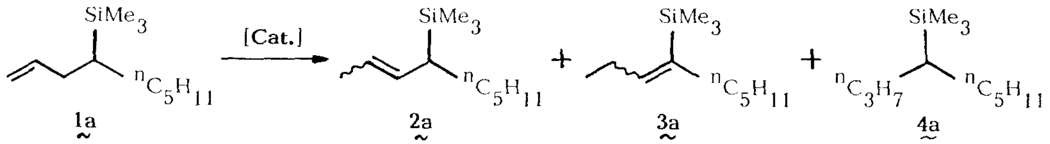


(1)

When a benzene solution of 4-trimethylsilyl-1-nonene (**1a**) and catalytic amount of $HRh(PPh_3)_4$ was heated for 7 h at 120 °C in a sealed tube, **1a** disappeared completely and four products, *E*-**2a**,[6] *Z*-**2a**,[6] *E*-**3a**,[6] and **4a** [6] were detected in the ratio of 73:21:5:2 which was evaluated by the GLC analysis. The result suggests that trimethylsilyl group can become the auxiliary to bring about remarkable energy difference among the regio isomers of olefin.

On the contrary 1-octene gave a complex mixture composed of almost all expected isomers under the analogous conditions. However, the formation of vinylsilane, *E*-3a as a byproduct was inevitable so long as neutral metal hydride were used as catalyst (Entry 1 ∿ 6 in Table 1). Although it is reported that vinylsilanes are more stable (Ca. 8 kJ/mole) than their allyl isomers,[8] allyltrimethylsilane was readily contaminated by isomerized product, 1-propenyltrimethylsilane, at 100 °C in the presence of catalytic amount of $HRh(PPh_3)_4$, $H_2Ru(PPh_3)_4$, or $HClRu(CO)(PPh_3)_4$. It suggests that lowering the reaction temperature is requisite for the selective formation of 2. However, the isomerization of 1 via the addition-elimination mechanism of M-H requires heating to some extent for complete conversion.

Thus, rhodium(I) and iridium(I) cationic complexes activated by small



(2)

Table 1. Isomerization of 1a. [a)]

Entry	Catalyst [b)]	Conditions Solvent	(°C/h)	Conversion (%)	Ratio of products [c)] *E*-2a	*Z*-2a	*E*-3a	4a
1	$HRh(PPh_3)_4$	C_6H_6	120/7	100	73	21	5	2
2	$HRh(PPh_3)_4$	C_6H_6	100/1	100	70	24	5	1
3	$HRh(PPh_3)_4$	C_6H_6	80/1	52	73	23	4	0
4	$H_2Ru(PPh_3)_4$	C_6H_6	105/1	100	66	31	1	2
5	$HClRu(CO)(PPh_3)_3$	C_6H_6	120/15	100	56	27	17	0
6	$HClRu(CO)(PPh_3)_3$	C_6H_6	105/1	100	70	29	1	0
7	$[Rh(NBD)(DPPB)]BF_4$	CH_2Cl_2	95/1	100	60	29	10	1
8	$[Rh(NBD)(DPPB)]BF_4$	CH_2Cl_2	55/1	100	76	20	1	3
9	$[Rh(NBD)(DPPB)]BF_4$	CH_2Cl_2	20/2	100	83	16	0	1
10	$[Rh(COD)(PPh_3)_2]PF_6$	CH_2Cl_2	20/2	83	92	6	0	2
11	$[Rh(COD)(PPh_3)_2]PF_6$	CH_2Cl_2	20/17	95	92	7	0	2
12	$[Ir(COD)(PPh_2Me)_2]PF_6$	CH_2Cl_2	20/2	100	86	9	0	6
13	$[Ir(COD)(PPh_2Me)_2]PF_6$	CH_2Cl_2	-20/2	100	87	6	0	8
14	$[Ir(COD)Py(PCy_3)]PF_6$	CH_2Cl_2	-20/2	76	74	10	0	16
15	$[Ir(COD)Py(PCy_3)]PF_6$	CH_2Cl_2	20/23	83	76	15	0	9
16	$[Ir(COD)(DPPB)]PF_6$	CH_2Cl_2	-20/2	13	77	0	0	24
17	$[Ir(COD)(PPh_3)_2]PF_6$	CH_2Cl_2	-20/2	100	97	0	0	3

a) Reactions were carried out on a 1 mmole scale in a sealed tube.

b) About 1 mol % of catalyst was used. Cationic complexes were activated by hydrogen before the addition of olefin. NBD; Norbornadiene, DPPB; 1,4-Bis-(diphenylphosphino)butane, COD; 1,5-Cyclooctadiene, Py; Pyridine, PCy_3; Tricyclohexylphosphine.

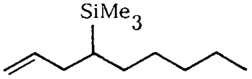
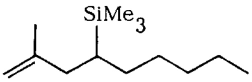
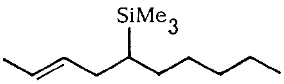
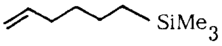
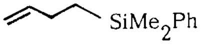
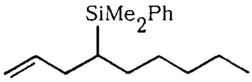
c) Determined by GLC analyses (OV 101 50 m column).

amount of hydrogen were used as a catalyst for isomerization of **1a**. The results are summarized in Table 1. The catalytic efficiency for the isomerization of **1a** depends on the ligands on metal. Iridium complex is more active than the corresponding rhodium one and the complete *E*-selectivity in the formation of **2** is attained by the catalysis of [Ir(COD)(PPh$_3$)$_2$]PF$_6$ (Entry 17 in Table 1).

Therefore the identical iridium complex was used as the catalyst in the isomerization of silylated olefins **1**. The results are summarized in Table 2. It should be noted that the stereochemical purity of **2** decreases in the internal double bond migration (Entry 3, 4, and 5 in Table 2) and that the migration of more than two bonds is possible (Entry 6 in Table 2). The phenyl group on silicon atom slightly affects the stereochemistry of the product and appreciably retards the rate of isomerization.

While it is difficult to rationalize the catalytic pathway of the present isomerization, the following observations suggest the presence of dinuclear complex **5** and HPF$_6$ in the early stage of the reaction[9];(A) it is essential for smooth isomerization of **1** to warm the solution of catalyst activated by hydrogen at -78 °C up to room temperature before the addition of **1** and (B) the

Table 2. Isomerization of 1 catalyzed by [Ir(COD)(PPh$_3$)$_2$]PF$_6$. a)

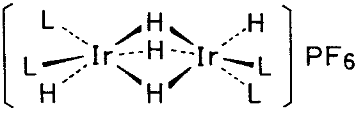
Entry	Silyl olefin **1**		Conditions (°C/h)	Yield (%)	Product Ratio b) *E*-**2**	*Z*-**2**	**4**
1		**1a**	-20/2	90	97	0	3
2		**1b**	20/1	94	100		0
3		**1c**	-78/3	60	81 c)	19	1
4			-20/1	90	86 c)	14	0
5			20/1	85	96 c)	3	1
6		**1d**	20/72	>95	80	15	4
7		**1e**	-40/0.7	97	80 c)	16	3
8		**1f**	25/3	85	81	7	8
9			100/5	96	96	0	4

a) Reactions were carried out on a 1 mmole scale in a sealed tube. The catalyst was activated by hydrogen before the addition of **1**.

b) Determined by GLC analyses (OV 101 50 m column).

c) Determined by GLC analyses (PEG-HT Bonded 25 m column).

addition of small amount of Et_3N to the solution of activated catalyst completely inhibits the isomerization of 1.



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6. These compounds were identified by the comparison of the ^{1}H NMR, IR, and GLC data with those of the authentic samples. A mixture of stereoisomers of 2 was prepared by a $NiCl_2$(DPPP) catalyzed Grignard coupling of the corresponding vinyl bromide and 1-trimethylsilylbutyl carbanion.[5a] A mixture of E-3 and the regio-isomer was prepared from p-toluenesulfonylhydrazone of the corresponding ketones.[7]
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