

Homogeneous Isomerization of 1-Butene Catalyzed by $[MX_2(PR_3)_2]-NaBH_4$ Systems ($M=Co, Ni$, $X=Halides, SCN$, $PR_3=PPh_nEt_{3-n}$)—Acceleration by Phosphine Addition and Stereoselectivity

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The stoichiometric or a little excess amount of $NaBH_4$ was treated with $[MX_2(PR_3)_2]$ ($M=Co, Ni$, $X=halides, SCN$, $PR_3=PPh_nEt_{3-n}$) in THF–1,2-dimethoxyethane to form monohydride species which were active for isomerization of 1-butene. The reaction was accelerated by excess PPh_3 in $[CoX_2(PPh_3)_2]-NaBH_4$ systems. Other catalytic systems have optimum ratios of excess phosphine to metal for getting maximum activities. Thiocyanate–metal complexes are the most active in each Co- and Ni-catalyst system. Cis-selectivity depends on the cone angle of PR_3 , the size of anion ligands, and the congested structure of complexes.

Double bond migration of linear terminal olefins is homogeneously catalyzed by many transition metal catalysts.¹⁾ Cocatalysts are frequently required: hydrogen,²⁾ acids,³⁾ and oxygenated compounds⁴⁾ have been used for heavy transition metal complexes to give metal hydrides. Alkylaluminum, Grignard reagents, and alkali metal alkyls and hydrides are effective cocatalysts for complexes of the first row transition metal complexes.⁵⁾

We have found the isomerization of 1-butene catalyzed by $[MX_2(PR_3)_2]$ ($M=Co, Ni$, $X=halogen, SCN, NO_3, CN$, $PR_3=PPh_nEt_{3-n}$) with sodium tetrahydroborate as a cocatalyst. One of characteristic features in these systems is that *cis*-2-butene is preferentially formed to the *trans*-isomer. Another is that the more PPh_3 is added, the more the rates of isomerization increase in the cobalt system. Since rates and stereoselectivity are dependent on halogen ligands, active species are cobalt or nickel hydrides containing Co–X or Ni–X bonding.

Experimental

Materials. The 1-butene which was purchased from Takachiho Chemicals had a purity of 99.8%. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (glyme) were refluxed over sodium and distilled before use. Cobalt and nickel halides were obtained from Nakarai Chemicals and used without purification. PPh_3 was recrystallized from methanol. Phosphines containing ethyl group were prepared by standard Grignard synthesis. $[CoX_2(PR_3)_2]$ ($X=halides, SCN$, $PR_3=PPh_nEt_{3-n}$, $n=0-3$) were prepared from cobalt halides and PR_3 in ethanol or acetone by the methods described in the literatures.⁶⁾ $[NiX_2(PR_3)_2]$ ($X=halides, SCN, NO_3, CN$) were similarly prepared from NiX_2 and phosphines in 1-butanol or ethanol according to the literatures.⁷⁾ Elemental analytical data of complexes

agree with those of calculated values.

Procedure and Analysis. Three ml of THF solution of a cobalt or a nickel complex (0.1 or 0.15 mmol) and 2 ml of glyme solution of $NaBH_4$ (0.025–0.1 mmol) were placed in each 10-ml ampule connected with each other. 1-Butene (4.2 mmol) was added to the ampules which were degassed and chilled in liquid nitrogen. After they were sealed and stored at 0 °C, two solutions were mixed and allowed to stand at 0 °C for a given interval. The reaction was stopped by freezing the solution in liquid nitrogen and the reaction mixture was distilled rapidly in vacuo. The distillate was analyzed by a Shimadzu-6A gas chromatograph on a column packed with 30% dimethylsulfolane on Celite 545 (5.6 m) at r.t. The concentration of $NaBH_4$ in glyme was determined by the titration with 1/100 N HCl using Methyl Red as an indicator.

Results

Formation of Metal Hydrides and Their Catalysis. Anhydrous cobalt chloride dissolved in THF was reacted with $NaBH_4$ at 0 °C to yield black precipitates. They had very little activity for isomerization of 1-butene. The presence of hydrogen caused isomerization but less rapidly compared to hydrogenation.⁸⁾

Cobalt halide complexes containing phosphine ligands such as $[CoCl_2(PPh_3)_2]$, were found to react with $NaBH_4$ to give green homogeneous solution, which effectively catalyzed isomerization of 1-butene. The rate of isomerization gradually decreased due to the decomposition of active species where cobalt metal began to be deposited. The decomposition was prevented by adding excess phosphine. A hydrogenated product, butane, was formed at the beginning of the reaction, but the amount did not increase with the elapse of time. The ratios of *cis*-2-butene to the *trans*-isomer (abbreviated as *c/t*) remain constant until 1-butene has almost been consumed. Scrambling of 2-butenes was much slower compared to double-bond migration.

Effects of the Concentration of $NaBH_4$ on the Isomerization of 1-Butene Catalyzed by $[CoX_2(PPh_3)_2]$ ($X=Halides, SCN$). Sodium tetrahydroborate is nec-

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essary for the formation of metal hydrides as active species. The effects of the ratio of NaBH_4 to cobalt complexes on the isomerization are shown in Fig. 1. In the case of $[\text{CoCl}_2(\text{PPh}_3)_2]$, the apparent rate, which is expressed as the conversion of 1-butene, increases proportionally with the increase of NaBH_4 . The reaction at $\text{H}^-/\text{Co}=4$ proceeded in suspension from the beginning. The initial state of the reaction mixture was homogeneous at $\text{H}^-/\text{Co} \leq 2$, and metal deposited at the end of the reaction at $\text{H}^-/\text{Co} \geq 1$. The c/t ratio was almost independent of H^-/Co ratios. The rates reach maxima at nearly stoichiometric concentration of NaBH_4 to produce monohydride in cases of $[\text{CoX}_2(\text{PPh}_3)_2]$ ($\text{X}=\text{Br}, \text{I}, \text{SCN}$). The c/t ratios remain constant when H^-/Co is less than 2, but

decrease at $\text{H}^-/\text{Co} > 2$.

The amounts of butane produced are nearly proportional to the concentration of NaBH_4 for any complexes. They decrease in the order $\text{Cl} > \text{Br} > \text{I} > \text{SCN}$ at the same ratio of NaBH_4 to the cobalt complex.

Similar effect of the NaBH_4 concentration was observed for $[\text{CoX}_2(\text{PPh}_n\text{Et}_{3-n})_2]$ ($n=0-2$) and $[\text{NiX}_2(\text{PPh}_n\text{Et}_{3-n})_2]$ ($n=0-3$) whereas H^-/M values giving maximum rates shift to somewhat higher ones than stoichiometry.

Effect of Addition of Excess Phosphine. The reaction mixture of Co-PPh_3 complexes at $\text{H}^-/\text{Co} \leq 2$ was kept homogeneous for several hours after which metallic precipitates began to be formed. The addition of excess PPh_3 kept homogeneity throughout the reaction and accelerated the isomerization (Fig. 1). The low values of c/t in Fig. 1 (the dotted lines) indicate the completion of double-bond migration of 1-butene followed by the scrambling of 2-butenes. The dependence of the rate on H^-/Co is the same with and without excess PPh_3 .

Rate Constants and Stereoselectivity in the Isomerization of 1-Butene Catalyzed by Co- and Ni-Phosphine Complexes. The isomerization was first order in 1-butene and the rates were proportional to the metal concentrations. The second-order rate constants, k' , are expressed as follows:

$$\frac{-d[1-\text{C}_4\text{H}_8]}{dt} = k[1-\text{C}_4\text{H}_8] \quad (1)$$

$$k = k'[\text{M}] \quad (2)$$

where $[\text{M}]$ stands for the concentration of metal complexes.

Cobalt catalysts, on the whole, are more active than nickel ones for the same ligands (Table 1, Fig. 2). $[\text{Co}(\text{SCN})_2(\text{PPh}_3)_2]-\text{NaBH}_4$ system is by far the most

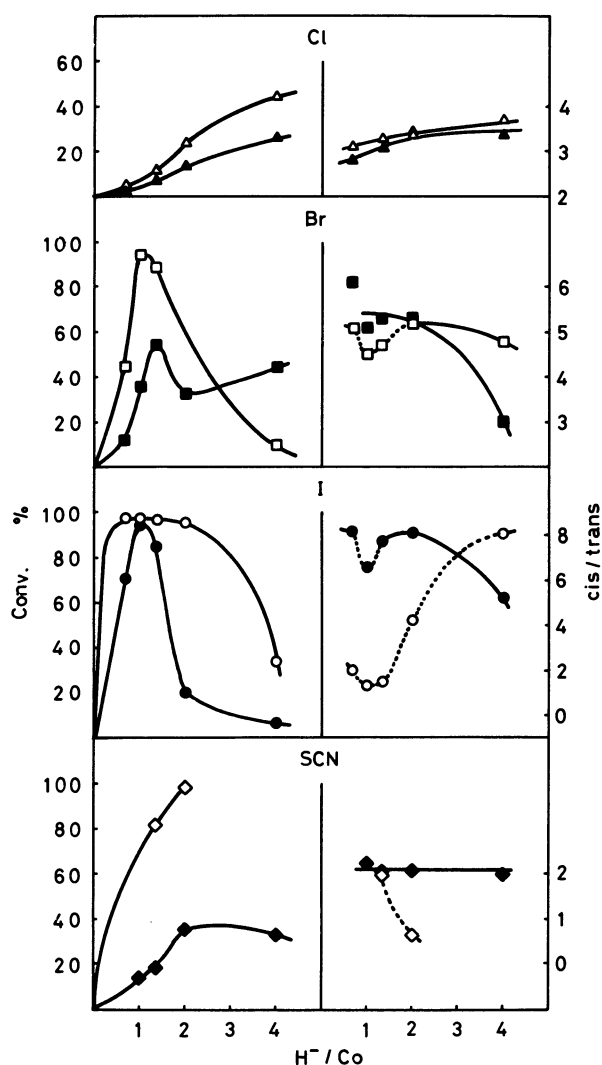


Fig. 1. The apparent rates and cis-selectivity of the isomerization of 1-butene by $[\text{CoX}_2(\text{PPh}_3)_2]-\text{NaBH}_4$ depend on the concentration of NaBH_4 . $[\text{Co}] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ ($\text{X}=\text{halogen}$), $8 \times 10^{-3} \text{ mol dm}^{-3}$ ($\text{X}=\text{SCN}$), $[1-\text{C}_4\text{H}_8] = 0.83 \text{ mol dm}^{-3}$. $\blacktriangle, \blacksquare, \bullet, \blacklozenge$: Without free PPh_3 ; $\triangle, \square, \circ, \lozenge$: free $\text{PPh}_3/\text{Co}=2$ ($\text{X}=\text{Cl}, \text{Br}, \text{SCN}$), 1.2 ($\text{X}=\text{I}$).

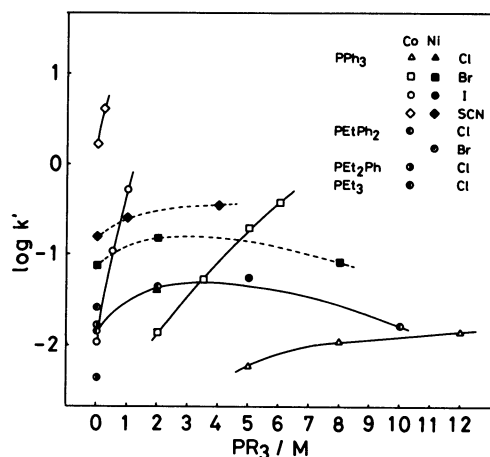


Fig. 2. Rate constants for the isomerization of 1-butene by $[\text{MX}_2(\text{PR}_3)_2]-\text{NaBH}_4$ systems as a function of the PR_3/M ratio.

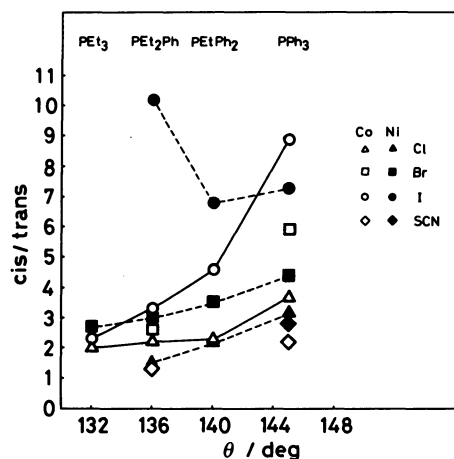


Fig. 3. Cis-selectivity depends on the cone angle of PR_3 .

active among them, where a very small amount of excess PPh_3 increases the rate. The same tendency is observed for $[CoI_2(PPh_3)_2]$ system. A large excess of PPh_3 never retards the isomerization for all Co- PPh_3 complexes. However, a small excess of PPh_3 increases the rate, but a large excess retards the isomerization for Ni- PPh_3 complexes. The rates decrease in the order $SCN > I > Br > Cl$ for cobalt catalysts, and $SCN > Br > I > Cl > NO_3$ for nickel catalysts. The substituents of ethyl group in PR_3 lower the rates and much more in nickel catalyst systems.

The c/t ratios which give a measure for stereoselectivity are dependent on both halogen and PR_3 ligands (Table 2, Fig. 3). The c/t ratio decreases in the order $I > Br > Cl > SCN$ for Co- PPh_3 catalysts, and

Table 1. Rate Constants in the Isomerization of 1-Butene Catalyzed by $[MX_2(PR_3)_2]-NaBH_4$ Systems¹⁾

M- PR_3	$k' \cdot 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				
	Cl	Br	I	SCN	NO_3
Co- PPh_3	0.59 ^d (5)	1.4 ^b (2)	1.1 ^b	170 ^d	
- PPh_2Et	1.4 ^d (12)	38 ^b (6)	52 ^b (1)	420 ^d (0.2)	
- $PPhEt_2$	1.4 ^b				
- $PPhEt_2$	4.4 ^b (2)				
- $PPhEt_2$	1.7 ^b (10)				
- PEt_3	1.2 ^b				
- PEt_3	1.7 ^d				
Ni- PPh_3	0.45 ^d				
- PPh_2Et	4.3 ^c (2)	7.3 ^c	2.9 ^c (2)	16 ^d	0.027 ^d
- PPh_2Et		15 ^c (2)	5.6 ^c (5)	26 ^d (1)	0.035 ^d (2)
- $PPhEt_2$		8.2 ^c (8)		36 ^d (4)	
- $PPhEt_2$	0.49 ^c	1.9 ^c	0.98 ^b		
- $PPhEt_2$	0.64 ^d		0.76 ^d		
- $PPhEt_2$	0.030 ^c	0.054 ^c	0.15 ^a		
- PEt_3		0.011 ^c	0.29 ^b		

1) $H/M = a$ 0.64, b 1.0, c 1.3, d 2.0. 2) The number in parentheses is the mole ratio of excess PR_3 to metal.

Table 2. Stereoselectivity in the Isomerization of 1-Butene Catalyzed by $[MX_2(PR_3)_2]-NaBH_4$ Systems

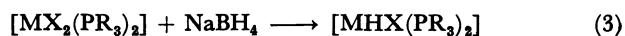
PR_3	$c/t^a) ((c/t)_x/(c/t)_{Cl})^b)$					
	Cl	Br	I	SCN	NO_3	CN
Co-catalysts						
PPh_3	3.7	5.9 (1.6)	8.9 (2.4)	2.2 (0.59)		
PPh_2Et	2.3		4.6 (2.0)			
$PPhEt_2$	2.2	2.6 (1.2)	3.3 (1.5)	1.3 (0.59)		
PEt_3	2.0		2.3 (1.2)			
Ni-catalysts						
PPh_3	3.2	4.4 (1.4)	7.3 (2.3)	2.8 (0.88)	3.4 (1.1)	2.0 (0.62)
PPh_2Et	2.2	3.5 (1.4)	6.8 (3.1)			
$PPhEt_2$	1.5	3.0 (2.0)	10.5 (7.0)			
PEt_3		2.7				

a) $cis-2-C_4H_8/trans-2-C_4H_8$. b) The number in parentheses is the ratio of c/t of a catalytic system to that of the chloro-catalyst system in M- PR_3 catalyst series.

I>Br>Cl>NO₃>SCN>CN for Ni-PPh₃ catalysts. Cis-selectivity increases with cone angle of PR₃ (Fig. 3). An exception is observed with [NiI₂(PPhEt₂)₂]-NaBH₄ system where the less stoichiometric ratio of H⁻/Ni gives high cis-selectivity. The increase of H⁻/Ni decreases the c/t ratio from 10.5 at H⁻/Ni=0.6 to 3.3 at H⁻/Ni=1. The effect of the change from Cl to Br and I on the cis-selectivity becomes less pronounced with the substituents of ethyl group of PR₃ for cobalt catalysts, but is magnified for nickel catalysts (numbers in parentheses in Table 2).

Discussion

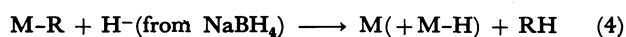
Active Species. The stoichiometric amount of NaBH₄ to form cobalt monohydride species gives maximum rates for the isomerization of 1-butene catalyzed by [CoX₂(PPh₃)₂]-NaBH₄ systems (X=Br, I) (Fig. 1). Active species should be metal hydrides containing halogen ligands since cis-selectivity of 2-butene is dependent on halogen ligands.



M = Co, Ni, X = halogen, SCN, PR₃ = PPh_nEt_{3-n}

Metal hydrides are stabilized by phosphines which act as σ-donors and π-acceptors.⁹ More basic phosphines strengthen M-H bonds¹⁰ to give less active catalysts. The coordination number of PR₃ is mostly two, but exceptionally three (vide post).

The isomerization has occurred through a metal-hydride addition and elimination mechanism. A small amount of butane was formed in the beginning of reactions. The amount of butane decreases in the order, Cl(33)>Br(22)>I(22)>SCN(10) for [CoX₂(PPh₃)₂], PPh₃(33)>PPh₂Et(16)>PPhEt₂(6)>PEt₃(8) for [CoCl₂(PR₃)₂] and does not change regularly with anion or PR₃ ligands (17–33) for [NiX₂(PR₃)₂] (the number in parentheses is the percentage of H⁻ (from NaBH₄) consumed into butane). No increase of butane during kinetic runs shows that butane was produced via Eq. 4 rather than Eq. 5.



Rate Enhancement and Retardation by Excess PR₃. Phosphines are very convenient and efficient ligands for many homogeneous catalytic reactions.¹¹ The disadvantages are susceptibility of orthometallation¹² and the inhibition of reactions by excess phosphines.^{13,14} Some reactions which need drastic conditions such as high temperatures contain excess phosphines to maintain catalytic species irrespective of lowering of rates.¹⁴ Many catalytic reactions by transition metal phosphine complexes are retarded by a small amount of phosphines.^{14,15} Here are presented two cases where (1) the more PR₃ is added,

the more the reaction is accelerated, and (2) an optimum addition of excess PR₃ gives a maximum rate as is often observed.

Acceleration of reactions by excess phosphines has been rarely observed.¹⁶ Cobalt(II) hydrides are too unstable to be isolated and identified due to thermal instability and lability.¹⁷ [CoX₂(PPh₃)₂] are originally tetrahedral.⁶ The stoichiometric amount of NaBH₄ reacts with [CoX₂(PPh₃)₂] to give monohydrido-substituted complexes.¹⁸ Since hydride is a strong σ-donor but halides are weak ones,¹⁹ monohydridocobalt complexes may change their structure into square planar one.²⁰ The active species should be bis(triphenylphosphine)cobalt complexes which holds the same stereoselectivity with and without free PPh₃. Excess PPh₃ can stabilize unstable cobalt hydrides which are easily decomposed by dissociation of PPh₃,^{6a,b} and prevent coupling of alkyl- and hydrido-metal complexes (Eq. 5). Accelerating effect per unit PPh₃ addition decreases in the order SCN>I>Br>Cl parallel to their soft character.²¹

Large excess of NaBH₄ gives [CoH₃(PPh₃)₃] in Ar,²² [CoH(N₂)(PPh₃)₃] in N₂,²³ and [Co(BH₄)(PPh₃)₂] and [Co(BH₄)(PPh₃)₃].¹⁷ These are assigned to be tri- and monovalent. [CoX(PPh₃)₃] forms on standing of [CoHX(PPh₃)₂] with PPh₃ in THF. A less bulky phosphine such as PMe₃ coordinates to Co(II) to give a five-coordinate complex, [CoMe₂(PMe₃)₃].²⁴ The reason why the third molecule of PPh₃ does not coordinate to halogenohydridocobalt(II) complexes is not obvious, but steric bulkiness of ligands may prevent further coordination.²⁵ In fact, excess of less bulky phosphine, PPh₂Et, hinders the isomerization catalyzed by cobalt chloride system.

A small amount of PPh₃ accelerates but large excess inhibits the reaction in [NiX₂(PPh₃)₂]-NaBH₄ systems. The c/t ratio of nickel iodide system drops at H⁻/Ni>1.3 due to the partial dissociation of PPh₃. The addition of 2 mol of PPh₃ maintains the c/t ratio of 7.3. However, large excess inhibits the reaction with the coordination site for 1-butene blocked by PPh₃.²⁶ Less reactivity of nickel systems may come from the strength of coordinated 1-butene onto the metal.²⁷ More basic phosphines retard the reaction and the tendency is pronounced for nickel catalyst systems. This is caused by the stability of hydrido and alkyl metal complexes as intermediates. Many σ-alkylnickel(II) complexes including PPh₃ were isolated and characterized,²⁸ but only a few alkylcobalt complexes with basic phosphines were identified.²⁰

Cobalt catalysts are more active than nickel ones for the complexes with the same ligands. On the contrary, [(η⁶-toluene)Ni(C₆F₅)₂] is a very active catalyst for 1-butene isomerization, but the analogous cobalt complex is not.²⁹ The electronic state of metals reflects the strength of metal-ligand bonds³⁰ leading to different reactivity. It is interesting that a metal

Table 3. Comparison of Stereoselectivity between Co- and Ni-Catalytic Systems

PR ₃	(c/t) _{Co} /(c/t) _{Ni}				
	Cl	Br	I	SCN	
PPh ₃	1.2	1.3	1.2	0.78	$\begin{array}{c} \uparrow \\ \pi\text{-acceptor} \\ \downarrow \\ \sigma\text{-donor} \end{array}$
PPh ₃ Et	1.0		0.68		
PPhEt ₂	1.5	0.87	0.32		
PEt ₃		0.78			
	$\xrightarrow{\text{soft}}$				

complex is active but another is not where they are isostructural. It is very hard to expect which metal complex is active or not.

Stereoselectivity. Bulky phosphines and large-sized anions lead high cis-selectivity in the cobalt catalyst systems similar to $[NiX(PPh_3)_3]$.¹⁵ Such tendency is not necessarily observed in the nickel catalyst systems. Nickel iodide complex with less bulky PPhEt₂ in the range of $H^-/Ni \leq 0.6$ gives the highest cis-selectivity among Ni-catalyst systems. This is due to congested $[NiHI(PR_3)_3]$ ^{26,31} which is formed from $[NiHI(PR_3)_2]$ and dissociated PR_3 . A similar congested complex, $[CoH(N_2)(PPh_3)_3]$, gives high cis-selectivity ($c/t=14$) in the isomerization of 1-pentene.³²

The atomic radius of cobalt is almost the same as that of nickel. The dependency of cis-selectivity on the metal (Table 3) is not due to the metal size. The strong σ -donor (the weak π -acceptor) character of phosphines and the soft character of anions lead the ratios, $(c/t)_{Co}/(c/t)_{Ni}$, less than unity. The electronic factor of these ligands may control stereoselectivity similar to the isomerization of 1-pentene with $[PdX_2(RCN)_2]$.³³

Some nickel(I) complexes might be formed analogously to cobalt complexes.³⁴ Nickel(I) complexes effectively catalyze isomerization of olefins,¹⁵ though cobalt(I) complexes do not. The c/t ratios in the isomerization of 1-butene catalyzed by $[NiX(PPh_3)_3]$ are 3.0, 3.7, and 8.1 for $X=Cl, Br, I$, respectively. The cis-selectivity is somewhat different from that by $[NiX_2(PPh_3)_2]-NaBH_4$ systems suggesting that Ni(I) species are rarely responsible for the reaction.

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