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Selective *cis*-Isomerization of 1-Pentene Catalyzed by Ni(I)-Triphenylphosphine Complexes

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Selective *cis*-isomerization of 1-pentene was carried out by $NiX(PPh_3)_3$ (X=halogen and pseudohalogen). First-order plots were obtained except for the iodo-complex. The addition of tin(II) chloride increased both activities and ratios of *cis*-2-pentene to the *trans*-isomer. Protic solvents accelerated the isomerization. Isotopic exchange between C_2D_4 and C_2H_4 or 1-pentene reveals that a metal hydride addition-elimination mechanism is operative.

We have previously reported that nickel complexes prepared *in situ* from $NiX_2(PPh_3)_2$ (X=halogen), PPh_3, and zinc catalyzed isomerization of 1-butene.[1] From the point of view that the isomerization activity and the ratio of *cis*-2-butene to the *trans*-isomer were dependent upon halides, we suggested that the catalytic species were Ni(I) complexes. A remarkable characteristic of the catalytic systems in the presence of $SnCl_2$ is the highest c/t ratio reported to date for the isomerization of terminal olefins catalyzed by transition metal complexes[2] and alkali-metal alkoxides.[3]

Halogenotris(triphenylphosphine)nickel(I) isolated from the above components has been found to be an active catalyst for isomerization of 1-pentene.[4] D'Aniello and Barefield[5] have confirmed that olefin isomerization by $NiX(PPh_3)_3$ occurred by a metal hydride pathway. The characteristics of the Ni(I) complexes in the isomerization of 1-pentene will be presented here in detail.

Experimental

Reagents. Tetrahydrofuran (THF) was refluxed over sodium, distilled, and stored in a nitrogen atmosphere. Methanol and ethanol were refluxed with sodium alkoxides and distilled. Triphenylphosphine was recrystallized from methanol. 1-Pentene was obtained from Tokyo Kasei Kogyo Co. and distilled prior to use. Other chemicals were commercial materials and used without further purification.

Nickel Complexes. Dihalogenobis(triphenylphosphine)-nickel(II) was prepared according to the method given in the literature.[6,7] A typical preparation of a Ni(I) complex was as follows. A mixture of 1.5 g (2 mmol) of $NiBr_2(PPh_3)_2$ and 0.61 g (2.3 mmol) of PPh_3 in 45 ml of benzene was treated with 0.65 g (10 mmol) of zinc dust. After a few minutes of stirring, the solution changed from green to yellow; it became red-brown and then the reaction mixture was rapidly filtered into a flask containing 0.02 g of $NiBr_2(PPh_3)_2$. When the solution turned yellow, the unreacted (undissolved) $NiBr_2(PPh_3)_2$ was removed by filtration. The filtrate was concentrated to one-third of its original volume. Thirty ml of methanol was added to the suspension to precipitate a yellow solid, which was collected and washed with five 10 ml portions of cold methanol. Drying *in vacuo* gave 1.55 g (82%) of $NiBr(PPh_3)_3$. Anal. Found: C, 70.09; H, 5.14. Calcd for $C_{54}H_{45}BrP_3Ni$: C, 70.10; H, 4.90 . $NiCl(PPh_3)_3$ and $NiI(PPh_3)_3$ were prepared in a similar manner; the yields were 61 and 46%, respectively. The elementary analyses supported the presence of Ni(I) complexes.[8]

Kinetics. The general procedure for the kinetic runs was as follows. A Ni(I) complex was weighed and added to a 100 ml flask. If an additive was used in a run, it was also weighed and added at this point. THF was vacuum distilled into the flask, which had already been evacuated and chilled in liquid nitrogen. The solvent was thawed and the mixture was stirred for 5 min to give a homogeneous yellow solution. After the mixture was again frozen in liquid nitrogen, 1-pentene was vacuum distilled into the flask. We determined the start of the isomerization to be when the mixture was thawed and stirred in a thermostated water bath at 0 °C.

Analysis. The concentrations of pentenes were followed by Shimadzu Model 2B and 4A gas chromatographs equipped with TCD and FID detectors. A 5.6 m×3 mm i.d. column packed with 60/80 mesh dimethylsulfolane (30%)/C-22 was operated at ambient temperature. Mass spectrometric analysis was made on a Hokushin time-of-flight mass spectrometer using an ionizing voltage of 12 eV.

Results and Discussion

Ligand Effects. When nickel complexes $NiX_2(PPh_3)_2$ (X=Cl, Br, I) were reduced with zinc in the presence of PPh_3 in THF or benzene, the green solution turned yellow and finally red-brown. The solutions contain a mixture of Ni(0) and Ni(I) species: the former is the red-brown species[9a] and the latter is the yellow one.[9b] The Ni(I) species was presumed to be an active catalyst for the isomerization of 1-butene.[1] This presumption has been confirmed by D'Aniello and Barefield on the basis of the isomerization of 1-butene-3,3-d_2 catalyzed by $(PPh_3)_3Ni(SnCl_3)$.[5] Since $NiX(PPh_3)_3$ was prepared by a disproportionation reaction between $Ni(PPh_3)_4$ and $NiX_2(PPh_3)_2$,[9b] it is expected that only $NiX(PPh_3)_3$ might be obtained when $NiX_2(PPh_3)_2$ is added by the amount equal to that of $Ni(PPh_3)_{3-4}$ formed in the reduction of $NiX_2(PPh_3)_2$ by zinc in the presence of PPh_3.[10] Our alternative method for the preparation of Ni(I) complexes is easy to carry out, without isolation of $Ni(PPh_3)_{3-4}$.

The first-order dependence on 1-pentene was observed without any induction periods at a 1-pentene/Ni ratio of 100, except for the iodo-complex, as shown in Fig. 1. Table 1 shows activities and c/t ratios for the isomerization of 1-pentene catalyzed by $NiX(PPh_3)_3$. Complexes with anion groups other than halogens were prepared *in situ* by replacing bromine on $NiBr(PPh_3)_3$ with KSCN, $NaOCH_3$, $AgPF_6$, and $AgClO_4$, respectively. The values in Table 1 show the results at the most favorable ratios of anions to $NiBr(PPh_3)_3$. Activities and c/t ratios are dependent upon anion ligands. Although large ions

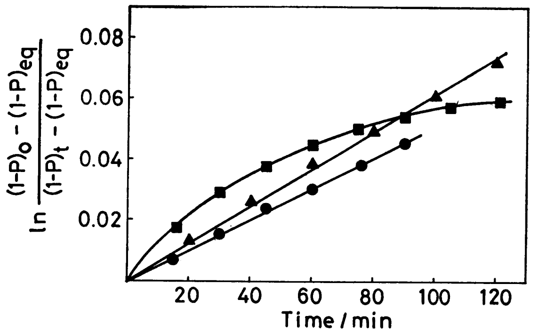


Fig. 1. Isomerization of 1-pentene catalyzed by $NiX(PPh_3)_3$.
●: Cl, ▲: Br, ■: I.

TABLE 1. RATES AND c/t RATIOS IN THE ISOMERIZATION OF 1-PENTENE WITH $NiX(PPh_3)_3$[a]

X	$\frac{k'}{10^{-3}\,s^{-1}\,M^{-1}}$	c/t
Cl	1.7 (3.9)[b]	2.99
Br	2.1 (5.8)[b]	4.11
I	—[c] (4.9)[b]	5.63
SCN(5.0)[d]	1.3	1.65
OCH_3(10)[d]	1.2	3.11
PF_6(1.2)[d]	0.83	3.45
ClO_4(1.1)[d]	13.5	4.15

a) [Ni] 5×10^{-3} M, [1-pentene] 0.48—0.5 M, THF 19 ml, 0 °C. b) Conv. after 80 min. c) A first-order plot was not observed. d) Complexes were prepared *in situ* by replacing Br on $NiBr(PPh_3)_3$ with KSCN, $NaOCH_3$, $AgPF_6$, and $AgClO_4$ at given mole ratios to Ni in solution.

such as PF_6^- and ClO_4^- form counterions to $[Ni(PPh_3)_3]^+$, the high activity of the ClO_4-complex compared with that of the PF_6-complex seems to be attributed to coordinatively unsaturated nickel species, according to the abstraction of PPh_3 by $AgClO_4$.[11]

Striking increases in activities and c/t ratios were observed in the presence of $SnCl_2$ as shown in Table 2. Both activities and c/t ratios increase with the amount of $SnCl_2$ and become constant at a $SnCl_2$/Ni ratio of nearly 100 in THF. The difference of maximum c/t ratios among halogen-systems can not be regarded as significant. However, the rates increase in the following order: I<Br<Cl. Since $Ni(SnCl_3)(PPh_3)_3$ is isolated by the reaction of $NiCl(PPh_3)_3$ with $SnCl_2$ in benzene,[5] the active species responsible for high activity is $Ni(SnCl_2X)(PPh_3)_3$, shown in Eq. 1. The difference of

$$NiX(PPh_3)_3 + SnCl_2 \rightleftharpoons Ni(SnCl_2X)(PPh_3)_3 \quad (1)$$

activity between halogen-systems might be attributed to that of the equilibrium constants. It is interesting to note that a first-order plot was obtained in the $NiI(PPh_3)_3$–$SnCl_2$ system, in contrast to the case of $NiI(PPh_3)_3$ alone. A small increase in rate and c/t ratio was observed at $SnBr_2/NiBr(PPh_3)_3$ ratios of 1/5—1/3, but a further addition of $SnBr_2$ retarded olefin isomerization.

Mixtures of $NiX_2(PPh_3)_2$ (X=Cl, Br) and $SnCl_2$ are less effective catalysts than $NiX_2(PPh_3)_2$ alone in the hydrogenation and isomerization of methyl linoleate.[7] This is because $SnCl_3$ ligand, which is a soft and π-acceptor one,[12] prefers soft metal ions such as Ni(I). Catalytic properties were greatly enhanced by replacing halogen ligands with $SnCl_3$ in the hydrogenation,[13–15] isomerization,[16–19] and hydroformylation.[20–22] The $SnCl_3$ group has a labilizing effect on other ligands, especially on a ligand *trans* to it,[23] which would facilitate the formation of a hydridonickel complex and activate Ni–H or Ni–alkyl bonds.

TABLE 2. THE EFFECTS OF THE ADDITION OF $SnCl_2$ ON THE ISOMERIZATION OF 1-PENTENE WITH $NiBr(PPh_3)_3$[a]

X	$SnCl_2$/Ni	$\frac{k'}{10^{-3}\,s^{-1}\,M^{-1}}$	c/t
Cl	16	24.3	15.4
	50	44.3	22.4
	99	50.3	29.1
Br	15	11.5	16.4
	58	26.3	22.5
	97	39.9	28.4
I	15	2.69	9.6
	49	11.5	10.1
	100	14.3	24.5

a) The reaction conditions were the same as those in Table 1.

TABLE 3. SOLVENT EFFECTS ON THE ISOMERIZATION OF 1-PENTENE WITH $NiBr(PPh_3)_3$[a]

X	Cosolvent	vol%	$\frac{k'}{10^{-3}\,s^{-1}\,M^{-1}}$	c/t
Cl	MeOH	21[b]	7.4	3.44
Br	MeOH	37	9.6	5.08
	CH_3CN	10[b]	11.8	2.92
	DMF	32[b]	3.1	3.66
	MEK	10	1.4	3.29
	Toluene	100	1.1	4.51
	H_2O	2.6[b]	24.6	4.48
I	MeOH	50	—(20.9)[c]	8.32

a) The reaction conditions were the same as those in Table 1. b) The vol% at which max rates were obtained. c) Conv. after 80 min.

Solvent Effects. A small difference of activity appeared between different lots. When the same lot was used in a series of experiments, the results were reproducible to ±10% on repeated runs so that they were discussed as indicating certain trends. Nickel(I) complexes are soluble in THF, aromatic hydrocarbons, DMF, and MEK, but less soluble in alcohols. Table 3 indicates solvent effects in the isomerization of 1-pentene catalyzed by $NiBr(PPh_3)_3$. None of the solvents are more suitable than THF as a one-component solvent. Maximum rates were observed at the vol% given in Table 3 for CH_3CN- and DMF–THF systems. Any amount of MEK retarded the isomerization. The c/t ratios decrease with the amount of aprotic solvents, which suggests that solvent molecules coordinate appreciably to the nickel atom. The addition of a small

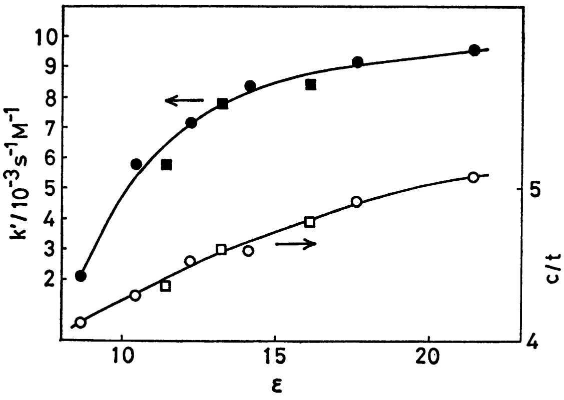


Fig. 2. Solvent effects on the rate and the *c*/*t* ratio in 1-pentene isomerization with $NiBr(PPh_3)_3$ in THF–alcohol system.
●, ○: MeOH, ■, □: EtOH.

amount of water led to a significant increase in activity and a slight increase in *c*/*t* ratio. An excess of water decreased both activity and *c*/*t* ratio, because the nickel(I) complex was caused to dissociate, which was followed by decomposition with butane evolution. The addition of methanol and ethanol led to the increase both in rates and *c*/*t* ratios, as was the case with water. Alcohols are precipitating agents for the nickel complexes, so that they are not added beyond a limited volume. Both the rate and *c*/*t* ratio increase with dielectric constants of THF–alcohol systems, as shown in Fig. 2. The color change was observed in protic solvent systems. The UV spectra showed λ_{max} at 343 nm ($\varepsilon=3.04\times10^3$) and 372 nm ($2.06\times10^3$) in THF, 345 nm ($4.08\times10^3$) and 370 nm ($2.79\times10^3$) in THF–MeOH, and 345 nm (4.51×10^3) and 372 nm (2.93×10^3) in THF–H_2O. Since the shifts of wavelength in λ_{max} are small, the change of the color is due to an increase of absorptivity. A similar acceleration by water or alcohols was observed in the codimerization of butadiene with ethylene catalyzed by σ-arylnickel(II) complexes–BF_3OEt_2.[24] Some complexes undergo oxidative addition of water as H and OH.[25] No results have suggested that protic solvents were used as a

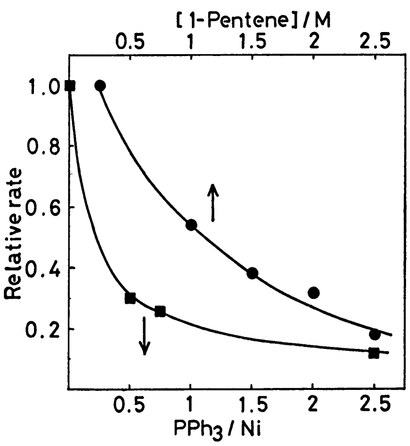


Fig. 3. Effects of excess PPh_3 and the concentration of 1-pentene on the rate of 1-pentene isomerization with $NiBr(PPh_3)_3$.

hydrogen source in our catalytic systems.

Effects of the Concentrations of Olefin and Free PPh_3. Figure 3 shows the effect of the concentlation of 1-pentene on the rate constants, where the relative rate constant is 1.0 at 0.25 M (1M=1 mol dm^{-3}) of 1-pentene. The rate constant decreases with an increase of the concentration of 1-pentene. Since no dimers of 1-pentene were observed, the retardation was due to the inhibitory impurities such as diene.[26] The presence of free PPh_3 slows activity because excess PPh_3 disturbs the coordination of olefins to the metal (Fig. 3).

Table 4. Dimerization of ethylene with $NiBr(PPh_3)_3$[a)]

Solvent	Temp °C	Time h	Conv. %	Composition 1-C_4H_8 %	Composition *c*/*t*
THF	0	71	1.1	88	4.7
THF[b)]	0	47	2.7	89	6.0
Toluene[c)]	30	25	1.3	79	4.1
Toluene–MeOH (4:1)	30	25	7.7	19	3.7
THF[c)]	30	25	1.4	81	4.1
THF–MeOH(4:1)[c)]	30	25	11	25	3.7

a) [Ni] 2—2.5×10^{-2} M, [C_2H_4] 0.2—0.25 M, Solvent 4—5 ml. b) $NiBr(PPh_3)_2$ was prepared *in situ* from the disproportionation between $Ni(C_2H_4)(PPh_3)_2$ and $NiBr_2(PPh_3)_2$. c) A small quantity of complex was decomposed into black metal.

Dimerization of Ethylene. The dimerization of ethylene was carried out with $NiBr(PPh_3)_3$, as shown in Table 4. Though the addition of methanol accelerated dimerization and isomerization, the activity of $NiBr(PPh_3)_3$ for dimerization was on the whole low. The active species for dimerization needs one more vacant site than that for isomerization. The conversion increased at high temperatures but complexes began to decompose to give black metal. The butene composition remains over 80% unless methanol is added.

Isotopic Mixing between C_2D_4 and C_2H_4 or 1-Pentene. Two mechanisms have been proposed in the isomerization of olefins.[27] The metal hydride addition-elimination mechanism which is most common is operative in catalysis by transition metal hydrides. The second involves oxidative abstraction of C–H of olefins to form a π-allylmetal hydride, or a vinylmetal hydride intermediate.[28] Since the second mechanism involves an intramolecular 1,3-shift of hydrogen, no hydrogen scrambling occurs between olefins.

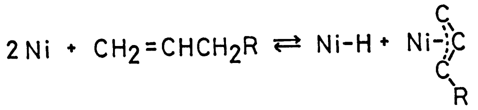
The exchange of hydrogen between C_2D_4 and C_2H_4 or 1-pentene was carried out to clarify the mechanism. Table 5 indicates: a) isotopic mixing between olefins occurs; b) the formation of metal hydride is less likely from the reaction of metal complexes and solvents; c) none of the ortho-hydrogen of PPh_3 is incorporated into olefins; d) a small amount of hydrogen from something other than olefins is incorporated into olefins. These results suggest that a metal hydride addition-elimination mechanism is operative. In this mechanism the hydride is produced from olefins *via* the reaction involving oxidative addition of an allylic

TABLE 5. ISOTOPIC MIXING BETWEEN C_2D_4 AND C_2H_4 OR 1-PENTENE CATALYZED BY Ni(I) COMPLEXES[a)]

Catalyst(mmol)		C_2D_4 (mmol)	C_2H_4 (mmol)	Time (h)	Isotopic distribution (%)						
Ni	$SnCl_2$				d_0	d_1	d_2	d_3	d_4	d_5	d_6
0.1		0.15	0.15	89	6.9	25.8	37.0	24.5	5.7		
0.1[b)]	1.0		0.49	89	100						
0.1[c)]	1.5		0.48	74	100						
0.1	1.1	0.27		64			0.6	7.2	92.2		
0.1	2.0	0.45	$1\text{-}C_5H_{10}$	70	30.3	39.9	19.0	2.9	7.9[d)]		
			0.45		8.3	23.1	31.0	20.9	11.2	4.2	1.0[e)]

a) Deuteroethylene (C_2D_4 96.9%, C_2D_3H 3.1%) was obtained from E. Merck Co. Reactions were done in 3 ml of THF at 0 °C. b) CD_3OD (0.5 ml) was added. c) $NiBr(PPh_3)_2(P(C_6D_5)_3)$ was used. d) The isotopic distribution of ethylene. e) The isotopic distribution of pentenes (1-pentene 6.1%, *trans*-2-pentene 17.8%, *cis*-2-pentene 76.1%). d_7 0.3%, d_8 0.05%.

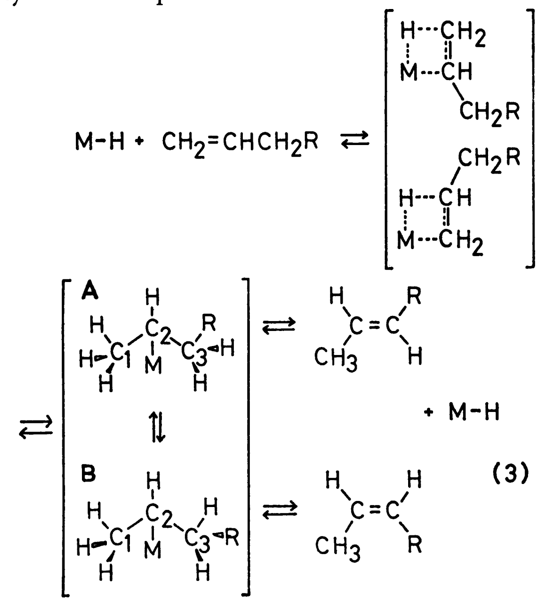
C–H bond of olefin to two Ni(I) centers, as D'Aniello and Barefield had confirmed.[5)] Vinylic hydrogen



(2)

would be abstracted from ethylene which has no allylic hydrogen. The low activity in the dimerization of ethylene is also attributed to the difficulty in breaking vinylic C–H bonds. The ease of hydrogen release from olefins was related to a decrease in the induction period and an increase in the rate of ethylene dimerization with $PdCl_2(PhCN)_2$.[29)] The absence of induction period in our systems indicates that a nickel hydride forms instantly. The equilibrium of Eq. 2 is responsible for the increase of nickel hydride with the amount of olefin. The opposite result (Fig. 3) suggests the inhibition is caused by the impurities.[26)]

Stereoselectivity. Selective *cis*-isomerization of terminal olefins was observed in base catalysts,[3)] $CoH(N_2)(PPh_3)_3$,[2)] and $NiX(PPh_3)_3$–$SnCl_2$ systems. The stereoselectivity in the base-catalyzed isomerization is explained by the result that the *cis*-allylic anion is thermodynamically more stable than the *trans* form.[3,30)] With a metal hydride catalyst, an olefin inserts into an M–H bond by a concerted reaction path to give σ-alkylmetal complexes:[31)]



(3)

When hydrogens bonded to C_3 approach the metal in a cyclic transition state, two structures are considered to have the C_3–R bond eclipsed and *gauche* with the C_2–H bond, as shown in **A** and **B**. The conformation of **A** is thermodynamically more stable than that of **B** for the steric repulsion between C_1 methyl and R groups, so long as the steric interaction between alkyl group and ligands is neglected. The bulkiness of ligands favors the conformation of **B** to give *cis*-2-olefins in the first-period transition metal catalyst systems: the *c*/*t* ratios decrease in the order I>Br>Cl, PPh_3>PPh_2Et>$PPhEt_2$>PEt_3 in the isomerization of 1-butene by $CoX_2(PR_3)_2$– and $NiX_2(PR_3)_2$–$NaBH_4$ systems (X= halogen, $PR_3=PPh_nEt_{3-n}$).[32)] The same trend is observed in the isomerization by $NiX(PPh_3)_3$. However, the opposite trend (Cl>Br>I) which was found in the isomerization of 1-pentene by $PdX_2(PhCN)_2$ was explained in terms of Pd–olefin stability.[33)] In the isomerization of 1-olefins catalyzed by Pt–$SnCl_3$ complexes, *trans*-2-olefins are formed preferentially.[16–19)] The high yield of *trans*-2-pentene was explained in terms of the stability of the eclipsed conformation of 2-pentyl radical coordinated to pseudo-planar platinum complex.[19)] The *cis*-selectivity in the Ni–$SnCl_3$ system is due primarily to the steric bulkiness of the $SnCl_3$ group thrusting away both C_1 methyl and R groups, as shown in **B** (Eq. 3). The bulk of the $SnCl_3$ ligand tends to favor the addition which leads to the sterically less hindered terminal-carbon–Pt complex in the hydroformylation of 1-olefins.[20)]

The π-acceptor ligands require square planar configurations rather than tetrahedral ones for four-coordinated nickel complexes. Since triphenylphosphine is bulky, $NiX(PPh_3)_3$ is forced to be tetrahedral because of steric repulsion between ligands.[9b)] If the active species are PPh_3–dissociated nickel complexes, the activated intermediates with π-acceptor ligands might be different from those with σ-donor ones such as halogen. Another effect of a π-acceptor ligand, $SnCl_3$, is to labilize the alkyl–metal bonds. Facile abstraction of β-hydrogen results in the formation of isomerized olefins before the interconversion of **A**⇄**B** in Eq. 3.

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