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Selective Isomerization of 1,5-Cyclooctadiene to 1,4-Cyclooctadiene Catalyzed by Bis(acetylacetonato)nickel–Triethyldialuminum Trichloride–Phosphorus Ligand

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The isomerization of 1,5-cyclooctadiene (1,5-COD) with Ni(acac)$_2$–Et$_3$Al$_2$Cl$_3$–phosphorus ligand (Ni : Al$_2$: P= 1 : 10 : 3) was first examined with varying P ligands in toluene in order to find suitable conditions for the formation of 1,4-COD. The product distribution depended largely on the P ligands. For several phosphites possessing very strong π-acceptor properties, the main product was 1,4-COD. In particular, the less-bulky bicyclic phosphite, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (**L-3**) was very effective and gave 1,4-COD in a high selectivity of 93% at 66% conversion (1,5-COD/Ni=500, molar ratio) by employing a low temperature of −30 °C. However, the reaction stopped before reaching completion because the catalyst was deactivated by the accumulation of 1,4-COD product. The conversion, depending on the 1,5-COD/toluene ratio (volume) rather than the 1,5-COD/Ni ratio, increased with a decrease in the 1,5-COD/toluene ratio and was 66—69% at a ratio of 0.19. On the other hand, the catalyst (P: **L-3**) was much less active for 1,4-COD than for 1,5-COD and was deactivated quickly under the same reaction conditions. This appeared to result in a high selectivity of 1,4-COD in the isomerization of 1,5-COD. The mechanistic implications of the experimental results are discussed.

The ordinary methods of preparation of 1,4-cyclooctadiene (1,4-COD) are either tedious$^{1)}$ or use rather expensive starting materials.$^{2)}$ Recently, selective isomerization of 1,5-COD to 1,4-COD with homogeneous transition-metal catalysts has been noted and investigated as a method of large-scale synthesis of 1,4-COD.$^{3)}$ In the isomerization, from the standpoints of the selectivity of 1,4-COD and its separation by fractional distillation, it is desirable to suppress the formation of the 1,3-isomer, which has a boiling point near that of 1,4-COD.

The isomerization of 1,5-COD to 1,4-COD and 1,3-COD has previously been attempted with homogeneous transition-metal catalysts, such as $PtCl_2(PPh_3)_2$–$SnCl_2 \cdot 2H_2O$,$^{4,5)}$ $PtCl_2(PPh_3)_2$–Ph_3SnCl,$^{6)}$ $Ru_2(1,5\text{-COD})_2(O_2CCF_3)_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}OH_2)$,$^{7)}$ $(\eta^5\text{-}C_5H_5)_2TiCl_2$–$i$-PrMgBr,$^{8)}$ $Ti(OBu)_4$–Et_3Al,$^{3)}$ or $Ru_3(CO)_{12}$$^{9)}$ (vide infra). A satisfactory yield of 1,4-COD, however, has not been obtained because of a subsequent rapid isomerization of 1,4-COD to 1,3-COD under the reaction conditions used. We have observed previously that Ni(acac)$_2$–Et$_3$Al$_2$Cl$_3$–phosphorus ligand, which forms an active nickel species, catalyzed the isomerization of 1,5-COD to bicyclo[3.3.0]oct-2-ene (BCO, transannular product), 1,4-COD, and 1,3-COD (double-bond isomerization product) and that the latter two products, especially 1,4-COD, increased with a decrease in the electron-donating ability of the phosphorus ligands.$^{10)}$ This observation prompted us to study the selective isomerization of 1,5-COD to 1,4-COD with this catalyst system. This paper details the results of our investigation.

Experimental

Materials. Toluene was purified by the ordinary method. 1,5-COD was distilled after drying over metallic natrium. Bis(acetylacetonato)nickel (anh.) and triethyldialuminum trichloride were obtained commercially.

Several phosphorus ligands, tris(p-chlorophenyl) phosphite,$^{11)}$ 2-phenoxy-1,3,2-dioxaphospholane,$^{12)}$ tri-o-tolyl phosphite,$^{11)}$ and diphenyl phenylphosphonite,$^{13)}$ were prepared according to the literature methods. Other phosphorus ligands were obtained commercially.

Reaction Procedure. A typical example is detailed below. In a 100 cm^3 flask fitted with a three-way stopcock and a thermometer were placed bis(acetylacetonato)nickel (25.7 mg, 0.10 mmol) and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (48.6 mg, 0.30 mmol). Liquid phosphorus ligands were added with 1,5-COD as a toluene solution. After replacing the air with nitrogen, a solution of 1,5-COD (5.41 g, 50 mmol) and propylbenzene (GLC internal standard) in toluene (30 cm^3) was added by syringe while stirring. The reaction was started by adding triethyldialuminum trichloride (1.0 mmol: 2.0 cm^3 of a 0.5 M (1 M=1 mol dm^{-3}) toluene solution) by syringe at −30 °C. The reaction mixture was kept at this temperature for 6 h. Small aliquots of the mixture were withdrawn, if necessary, during the course of the reaction and treated with a methanol–aqueous hydrochloric acid mixture. The organic layer was then separated and subjected to GLC analysis.

Analysis. The gas chromatographic analysis was made by a Shimadzu-GC-4AIT with a TC detector and He carrier gas using a 9-m PEG-20M column at 80 °C.

Results and Discussion

Effect of the Phosphorus Ligands. The isomerization of 1,5-COD with Ni(acac)$_2$–Et$_3$Al$_2$Cl$_3$–P ligand (Ni : Al$_2$: P=1 : 10 : 3 molar ratio) was carried out at −30 °C and 10 °C in toluene. Various phosphites having π-acceptor properties were used as phosphorus ligands in view of the results of our previous work.$^{10)}$ The results

Table 1. Effect of Phosphorus Ligands[a]

Ligand	ν_{CO}[b]/cm^{-1}	θ[b]/deg	Temp/°C	Time/h	Conversion[c]/%	Selectivity[d]/%		
						1,4-COD	1,3-COD	BCO
$P(OCH_2CF_3)_3$ (L-**1**)	2095.4[e]	110[e]	20	6	50 (22)	68	7	25
			−30	6	48 (3)	89	7	5
$P(O\text{-}p\text{-}C_6H_4Cl)_3$ (L-**2**)	2089.3	128	10	6	34[h] (21)	61	3	35
			−30	6	32 (1)	91	5	4
$P(OCH_2)_3CEt$ (L-**3**)	2086.8	101	10	1.5	54[h] (48)	90	5	6
			−30	6	66[h] (24)	93	6	1
$P(OCH_2)_2OPh$ (L-**4**)	2086.5	114[f]	10	6	45[h] (7)	30	3	66
			−30	6	68 (2)	78	12	11
$P(OPh)_3$ (L-**5**)	2085.3	128	10	1.5	23[h] (16)	67	3	30
			−30	6	24 (3)	81	5	14
$P(O\text{-}o\text{-}C_6H_4Me)_3$ (L-**6**)	2084.1	141	10	1.5	26[h] (18)	70	3	27
$PPh(OPh)_2$ (L-7)	2079.8	129[g]	10	1	89 (10)	12	2	86
$P(OEt)_3$ (L-**8**)	2076.3	109	10	1.5	97 (18)	2	0	98
			−30	6	7(1)	5	0	95
PPh_3 (L-**9**)	2068.9	145	10	1.5	97 (7)	1	0	99
None			10	1.5	100(8)	1	0	99

a) 1,5-COD, 50 mmol; $Ni(acac)_2$, 0.1 mmol (Ni:Al_2:P=1:10:3); Toluene, 32 cm^3, including 2 cm^3 of 0.5 M toluene solution of $Et_3Al_2Cl_3$. b) From Ref. 14 unless otherwise noted. c) Values in parentheses are conversions at 5 min. d) Selectivity of 1,4-COD is defined as 100×[1,4-COD]/([1,4-COD]+[1,3-COD]+[BCO]). e) P. W. N. M. van Leeuwen and C. F. Roobeek, *Tetrahedron,* **37**, 1973 (1981). f) Value for $P(OMe)_2OPh$. g) P. Heimbach, J. Kluth, H. Schenkluhn, and B. Weimann, *Angew. Chem., Int. Ed. Engl.,* **19**, 569 (1980). h) The reaction stopped practically at the conversions.

are shown, together with $\nu_{CO}(A_1)$ of $Ni(CO)_3L$ and the cone angle (θ) of the P ligands,[14] in Table 1. The effect of the P ligands on the product distribution was remarkable at both temperatures of −30 and 10 °C. Of the various P ligands used, a bicyclic phosphite, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (L-**3**), which has the smallest cone angle (θ=101°) and comparatively weak electron-donating ability (ν_{CO}=2086.8 cm^{-1}), gave the best result. At −30 °C, the selectivities of 1,4-COD, 1,3-COD, and BCO were 93, 6, and 1%, respectively, with 66% conversion. It was particularly noteworthy that the subsequent isomerization of 1,4-COD to 1,3-COD was suppressed satisfactorily.

Judging from the ν_{CO} values, strong π-acceptor ligands L-**1**—**6**, which have ν_{CO} values higher than 2084 cm^{-1}, gave 1,4-COD at the major product, while weaker π-acceptor ligands L-**7**—**9** and no ligand gave BCO as the major product.[15] On the other hand, the small cone angle of the ligand favors the formation of 1,4-COD, as indicated by the results with ligands L-**3** (ν_{CO}=2086.8 cm^{-1}, θ=101°) and L-**4** (ν_{CO}=2086.5 cm^{-1}, θ=114°) which have almost the same ν_{CO} values. In conclusion, P ligands such as L-**1** and L-**3**, which are less bulky and have strong π-acceptor abilities, appear to facilitate the formation of 1,4-COD.

With ligands L-**1**—**6**, however, the reaction stopped before reaching completion, e.g., only 66% conversion with ligand L-**3** at −30 °C. Although the rate of the isomerization to 1,4-COD was generally fast at the initial stage, as seen by the values of the conversion at 5 min (Table 1, Footnote c), it dropped rapidly and the reaction stopped prematurely. This termination was found to occur at especially low conversions in the cases of triaryl phosphite-type ligands L-**2**, **5**, and **6** which have relatively large cone angles.

Effect of Temperature and Time. The isomerization was carried out at temperatures ranging from 10 °C to −50 °C in toluene using L-**3** as the P ligand. These results are shown in Table 2. The reaction proceeded more rapidly in the early stages at higher temperatures, as indicated by the variations of conversion with time, but stopped before reaching completion in all runs. For example, the conversion at −30 °C (Run 3) stopped at about 65% for the times ranging from 4 to 6 h, though reaching 62% in just 2 h. In the temperature range of 10 to −30 °C, the conversion of 1,5-COD increased with a decrease in the temperature from 52% at 10 °C to 66% at −30 °C. At the lower temperature of −50 °C, however, the conversion was less than 50% (Run 4). Additionally, the selectivity of 1,4-COD at about 50% conversion increased with a decrease in the temperature from 90% at 10 °C to 96% at −50 °C. This was due largely to the decrease in the formation of BCO. With respect to the values of both the conversion and the selectivity, −30 °C appeared to be the most suitable temperature. The variation of the conversion of 1,5-COD and the selectivity of 1,4-COD with time at −30 °C showed that the isomerization of 1,4-COD to 1,3-COD proceeded much more slowly compared with that of 1,5-COD to 1,4-COD, and that both the isomerizations stopped at almost the same time. It was noteworthy that the Ni–Al_2–L-**3** catalyst favorably suppressed the isomerization of 1,4-COD to 1,3-COD even at a fairly high conversion of 66%, in contrast to several transition-metal complex catalysts previously reported[3–9] (See Table 4). Allinger et al.,[16] who investigated the isomer-

Table 2. Effect of Temperature and Time[a)]

Run	Temp/°C	Time/min	Conversion/%	Selectivity/%		
				1,4-COD	1,3-COD	BCO
1	10	30	51	90	5	6
		60	52	90	5	6
2	−10	30	57	92	5	3
		120	58	92	5	3
3	−30	5	24	98	1	1
		30	43	97	3	1
		120	62	94	5	1
		240	65	93	5	1
		360	66	93	6	1
4	−50	240	42	96	3	1
		360	46	96	4	1
5[b)]	−30	120	69	77	17	6
		360	75	73	20	7

a) 1,5-COD, 50 mmol; $Ni(acac)_2$, 0.1 mmol ($Ni:Al_2:L\text{-}3=1:10:3$); Toluene, 32 cm^3. b) Dichloromethane (30 cm^3) was used as solvent.

Table 3. Effect of Amounts of 1,5-COD and Catalyst[a)]

Run	1,5-COD/mmol	Ni/mmol	Toluene/cm^3	1,5-COD/Ni	1,5-COD[b)]/Toluene	Conversion/%	Selectivity of 1,4-COD[c)]/%	Catalyst turnover[d)]
3	50	0.1	32	500	0.19	66	93	307
6	50	0.2	32	250	0.19	69	92	159
7	100	0.1	32	1000	0.38	52	93	484
8	100	0.2	32	500	0.38	54	95	257
9	100	0.2	14	500	0.88	37	95	176
10	100	0.2	3.5[e)]	500	3.5	16	95	76
11	6	0.1	32	60	0.023	80	81	39

a) $Ni:Al_2:L\text{-}3=1:10:3$; Temp, −30 °C; Time, 6 h. b) Volume ratio. c) See Note c) in Table 1. d) Defined as [1,4-COD]/[Ni]. e) From 4 cm^3 of a 0.5 M toluene solution of $Et_3Al_2Cl_3$.

ization equilibrium of the cyclooctadienes, reported that the equilibrium composition in dimethyl sulfoxide at 70 °C is <0.01% 1,5-COD, 0.5% 1,4-COD, and 99.5% 1,3-COD. We have found that the nickel catalyst is not very active in the isomerization of 1,4-COD to 1,3-COD and , in addition, is probably deactivated by the accumulation of 1,4-COD to result in a practical stop of the isomerization of 1,5-COD to 1,4-COD. As an apparent phenomenon concerning the deactivation, it was observed that the color of the reaction mixture changed from its initial reddish-brown to pale yellow as the reaction approached termination.

The use of other solvents was also investigated. With dichloromethane as solvent, the conversion of 1,5-COD increased to 75%, but the selectivity of 1,4-COD decreased to 73%, the selectivities of 1,3-COD and BCO being 20 and 7%, respectively (Table 2, Run 5). With THF as solvent, the isomerization did not occur.

Effect of the Amounts of 1,5-COD and Catalyst. The P ligand L-3 gave a high selectivity of 1,4-COD, but the reaction stopped at a certain degree of conversion, as described above. In an attempt to increase the degree of conversion, the isomerization was performed at various 1,5-COD/Ni molar ratios and 1,5-COD/toluene volume ratios at −30 °C (Table 3). In all cases, the reaction stopped after several hours without reaching completion, though 1,4-COD was formed in selectivities higher than 92% (except for Run 11 which was carried out in a very dilute solution). When the reaction was performed using 50 mmol of 1,5-COD in 32 cm^3 of toluene (1,5-COD/toluene=0.19), the conversions and catalyst turnovers were 66% and 307 with 0.1 mmol Ni (Run 3), and 69% and 159 with 0.2 mmol of Ni (Run 6), respectively. It is noteworthy that irrespective of the catalyst amount, the conversions are almost the same and the catalyst turnover in the former reaction was about twice that in the latter. A similar result was also observed in the case in which the amount of 1,5-COD was increased from 50 to 100 mmol (1,5-COD/toluene ratio=0.38). The conversions and catalyst turnovers were 52% and 484 with 0.1 mmol of Ni (Run 7), and 54% and 257 with 0.2 mmol of Ni (Run 8), respectively. Thus, it was concluded that the conversion of 1,5-COD did not greatly increase with an increase in the catalyst amount.

On the other hand, the conversion appears to be influenced largely by the dilution of 1,5-COD with toluene, namely, the 1,5-COD/toluene ratio. In fact,

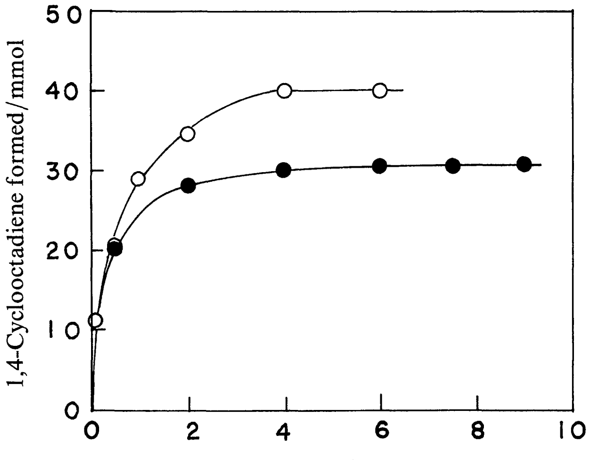


Fig. 1. Addition of 1,5-cyclooctadiene during the course of reaction. Reaction conditions: 1,5-COD, 50 mmol; Ni(acac)$_2$, 0.1 mmol (Ni : Al$_2$: L-3=1 : 10 : 3); Toluene, 32 cm^3; Temp, −30 °C. ○: After 0.5 h 50 mmol of additional 1,5-COD was added. ●: After 6 h 50 mmol of additional 1,5-COD was added.

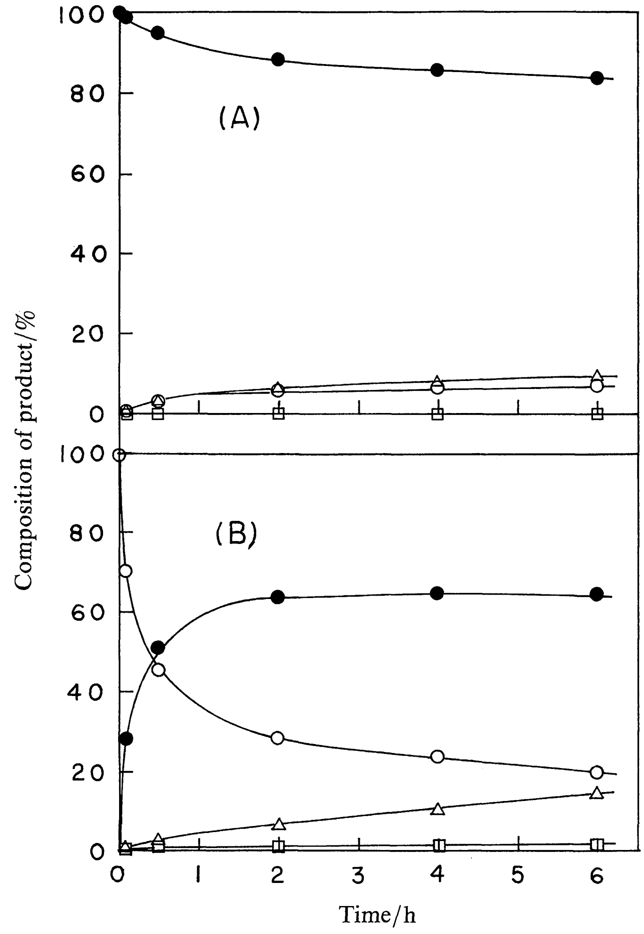


Fig. 2. Isomerization of 1,4- and 1,5-cyclooctadienes. (A): From 1,4-COD; (B): From 1,5-COD. Reaction conditions: COD, 6 mmol; Ni(acac)$_2$, 0.1 mmol (Ni : Al$_2$: L-3=1 : 10 : 3); Toluene, 32 cm^3; Temp, −30 °C. ●: 1,4-COD; ○: 1,5-COD; △: 1,3-COD; □: BCO.

the conversion decreased with an increase in the 1,5-COD-toluene ratio, being 66, 54, and 37% at ratios of 0.19, 0.38, and 0.88, respectively, in the case of 1,5-COD/Ni=500 (Runs 3, 8, and 9). Furthermore, when the ratio was 3.5 (no additional toluene was added, only the 0.5 M toluene solution of Et$_3$Al$_2$Cl$_3$ was used), the conversion remained at only 16% (Run 10). Conversely, a very dilute solution with a ratio of 0.023 gave a high conversion of 80% (Run 11). From the above results, we have concluded that toluene as solvent contributes to the stabilization of the catalytically active nickel species (vide infra) to result in a higher conversion at a lower 1,5-COD/toluene ratio and that the accumulation of 1,4-COD product deactivates the catalyst. In order to confirm the deactivation of the catalyst, an attempt was made to add additional 1,5-COD to the reaction. The reaction was started under the same conditions as those for Run 3 (Fig. 1). When additional 1,5-COD was introduced after 6 h, at which time the reaction had practically stopped, no further isomerization was observed. On the other hand, when additional 1,5-COD was added after 30 min of reaction, 1,4-COD was obtained in a larger amount than that obtained in the former additional reaction. We interpret this to mean that after 6 h, the catalytically active species are no longer present. Thus, the termination of the reaction is not due to an equilibrium between 1,5-COD and 1,4-COD,[17] but to the deactivation of the catalyst.

The Characteristics of the Catalyst. The isomerization of 1,4-COD with the Ni–Al$_2$–L-**3** catalyst was investigated in comparison with the isomerization of 1,5-COD (Fig. 2). In both cases, the reaction had stopped practically after 6 h. The conversion of 1,4-COD at that time was only 16% in contrast to 80% cnversion for 1,5-COD. The ratio of the relative initial rates of 1,4-COD to 1,5-COD, calculated based on the conversions at 5 min, was about 0.04. These data, together with the results of the isomerization of 1,5-COD, indicated that the catalytically active species was much less active for 1,4-COD than for 1,5-COD and was rapidly destroyed by the accumulation of the 1,4-COD product.[18] In addition, it was noteworthy that 1,4-COD isomerized to the better-chelating 1,5-COD at almost the same initial rate as that of its isomerization to 1,3-COD (Fig. 2-(A)). As a result, the catalyst suppressed the isomerization of 1,4-COD to 1,3-COD to result in a highly selective isomerization of 1,5-COD to 1,4-COD. Several investigations on the isomerization of 1,5-COD to 1,4-COD are summarized in Table 4. Since the 1,4-COD product isomerizes rapidly to 1,3-COD with catalysts other than ours, the selectivities of 1,4-COD at 45—66% conversions are shown for comparison. With our catalyst, the selectivity was especially high compared with the selectivities of the others. Furthermore, good suppres-

Table 4. Summary of Several Investigations

Catalyst system	Solvent	1,5-COD[a] / Catalyst	Temp / °C	Time / min
$\mathrm{Ni(acac)_2{-}Et_3Al_2Cl_3{-}P(OCH_2)_3CEt}$	PhMe	500	−30	240
$\mathrm{PtCl_2(PPh_3)_2{-}SnCl_2{\cdot}2H_2O{-}H_2}$	$\mathrm{CH_2Cl_2}$	1000	75	240
$\mathrm{PtCl_2(PPh_3)_2{-}Ph_3SnCl{-}H_2}$	$\mathrm{CH_2Cl_2}$	150	120	30
$\mathrm{Ru_2(1,5\text{-}COD)_2(O_2CCF_3)_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}OH_2)}$	THF	100	45	20
$\mathrm{(\eta^5\text{-}C_5H_5)_2TiCl_2}$-*i*-PrMgBr	$\mathrm{(Et_2O)}$[e]	200	25	15
$\mathrm{Ti(OBu)_4{-}Et_3Al}$	None	800	100	70
$\mathrm{Ru_3(CO)_{12}}$	*n*-$\mathrm{C_8H_{18}}$	200	125	30
$\mathrm{Ru_3(CO)_{12}/SiO_2}$[f]	*n*-$\mathrm{C_8H_{18}}$	200	70	45

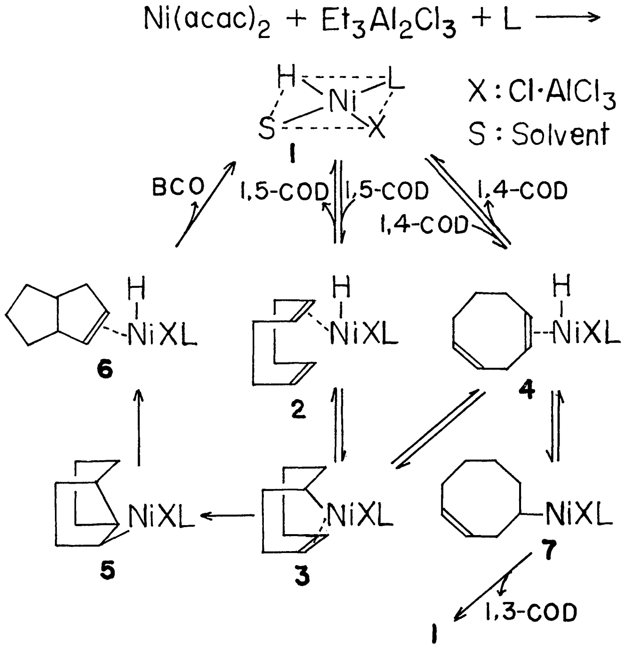
Catalyst system	Composition of Product[b]/% 1,5-COD	1,4-COD	1,3-COD	BCO	Selectivity of 1,4-COD[c]	Reference
$\mathrm{Ni(acac)_2{-}Et_3Al_2Cl_3{-}P(OCH_2)_3CEt}$	35	60	4	1	93	This paper
$\mathrm{PtCl_2(PPh_3)_2{-}SnCl_2{\cdot}2H_2O{-}H_2}$	36	42	22	0	66	4, 5)
$\mathrm{PtCl_2(PPh_3)_2{-}Ph_3SnCl{-}H_2}$	54	34	11	0[d]	76	6)
$\mathrm{Ru_2(1,5\text{-}COD)_2(O_2CCF_3)_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}OH_2)}$	51	20	29	0	41	7)
$\mathrm{(\eta^5\text{-}C_5H_5)_2TiCl_2}$-*i*-PrMgBr	50	30	20	0	60	8)
$\mathrm{Ti(OBu)_4{-}Et_3Al}$	55	30	15	0.5	66	3)
$\mathrm{Ru_3(CO)_{12}}$	50	23	27	0	46	9)
$\mathrm{Ru_3(CO)_{12}/SiO_2}$[f]	34	35	31	0	53	9)

a) Molar ratio. b) Taken at 45—66% conversions. c) See Note c) in Table 1. d) Cyclooctene was formed in a trace amount. e) From a small amount of *i*-PrMgBr-ether. f) Heterogenized catalyst.

sion of the formation of 1,3-COD is favorable for the isolation of 1,4-COD by distillation,[3,19] because the boiling points of 1,5-COD (150.8 °C/755 mmHg (1 mmHg=133.322 Pa)), 1,4-COD (145.1 °C/758 mmHg), and 1,3-COD (142.7 °C/754 mmHg),[20] (and especially of the latter two), are close to each other.

Mechanistic Implications. In general, the catalyst $\mathrm{Ni(acac)_2{-}Et_3Al_2Cl_3}$–P ligand, which in situ generates a specific square planar nickel hydride complex **1**, operates by the addition and elimination of a Ni–H function in double-bond migration.[21] A reaction mechanism, being essentially the same as that described in our previous paper,[10] is proposed to account for the experimental results (Scheme 1). The Ni–H species **1** may coordinates 1,5-COD[22] which then undergoes insertion into the Ni–H bond and subsequent coordination of the second double bond to give a σ, π-cyclooctenyl nickel complex **3**. In complex **3**, a β-H elimination reaction and an intramolecular insertion reaction take place competitively to result in double-bond isomerization (complex **4**) and cyclization (complex **5**) of 1,5-COD, respectively. The isomerization/cyclization ratio depends primarily on the P ligands.[10] The η^2-1,4-COD complex **4** gives 1,4-COD and **1**, and the catalytic cycle recurs.

The Ni–H species **1** with weak σ-donor P ligands may be normally unstable and ineffective for the isomerization of common olefins. In practice, 1,4-COD was only slightly isomerized with the Ni–Al$_2$–L-**3** catalyst, as shown in Fig. 2-(A), but 4-methyl-1-pentene was not isomerized at all.[18] With 1,5-COD, however, complex **3** would be stabilized by coordination of the second double bond to act as an intermediate in the isomerization of 1,5-COD. In view of the high selectivity of 1,4-COD, it seems likely that the coordinate double bond in **3** is not adequately activated with strong π-acceptor P ligands and therfore **3** undergoes Ni–H elimination in preference to intramolecular insertion. In addition, the less bulky phosphite L-**3** appears to favor the formation of complex **4**, which has a more crowded environment



Scheme 1. Reaction mechanism.

around the nickel than does complex **5**, compared with bulky phosphites such as L-**4** and L-**5** having almost the same ν_{CO} values. Then, complex **4** would give complex **2** rapidly via the dissociation of 1,4-COD if 1,5-COD exists in large amounts and the double bond in **4** coordinates weakly to the nickel. Thus, the use of strong π-accepting and less bulky phosphites may lead to the highly selective isomerization of 1,5-COD to 1,4-COD.

Next, the deactivation of the catalyst caused by the accumulation of 1,4-COD will be discussed in some detail. In the isomerization of 1,5-COD, while the 1,5-COD/1,4-COD ratio is large, complex **4** may transfer to the stabilized complex **3**, via complex **2** rather than complex **7**. As 1,4-COD is produced with subsequent 1,5-COD depletion, however, the ratios of complexes **4** and **7** to total active nickel species would increase. This seems to relate to the deactivation of the catalytic species in view of the fact that the isomerization of 1,4-COD with the Ni–Al_2–L-**3** catalyst stops at a very low conversion, as described above. However, the deactivation process is not clear at the present time. As a possible process, it may be proposed that, besides undergoing normal β-elimination, complex **7** is converted to the inactive nickel species Ni[L-**3**]$_n$, 1,3-COD, and HX by the action of L-**3**.[23] Consequently, this conversion could result in the termination of the reaction and the suppression of 1,3-COD formation.

Concerning solvents, suitable ones such as toluene and dichloromethane may participate in stabilizing the catalytically active species, in contrast to THF in which the isomerization does not proceed. Therefore, high dilution of 1,5-COD with toluene along with low reaction temperature would bring about its high conversion to 1,4-COD.

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15) In this connection, it has been reported that the isomerization of 1,5-COD can be directed to almost complete formation of 1,3- and 1,4-COD by employing trimethylphosphine (ν_{CO}=2064 cm^{-1}, θ=118°) as P ligand and that it is possible, by terminating the reaction before completion, to isolate 1,4-COD in up to 40% yield (B. Bogdanović, "Selectivity Control in Nickel-Catalyzed Olefin Oligomerization," in "Advances in Organometallic Chemistry," ed by F. G. A. Stone and R. West, Academic Press, New York (1979), Vol. 17, p. 105). Therefore, the use of PMe_3 was attempted under our conditions. The result was considerably different from that reported by Bogdanović, but it was observed that PMe_3 gave 1,4-COD in a moderate selectivity of 49%, together with BCO in 45% selectivity, at 48% conversion at 10 °C, in contrast with other trialkylphosphines such as PEt_3 and PBu_3.[10]

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17) It has been reported that the isomerization of 1,5-COD to 1,4-COD catalyzed by $Ir_2H_2Cl_2$(1,5-COD) is reversible (M. Gargano, P. Giannoccaro, and M. Rossi, *J. Organomet. Chem.*, **84**, 389 (1975)).

18) Furthermore, the isomerization of an alkene, 4-methyl-1-pentene, with the catalyst Ni–Al_2–L-**3**, was attempted for reference. We found that the catalyst did not have the ability to isomerize the olefin, in contrast with the Ni–Al_2–PPh_3 (L-**9**) catalyst (Y. Sakakibara, M. Mukai, M. Sakai, and N. Uchino, *Nippon Kagaku Kaishi*, **1972**, 1457).

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22) In the 1,5-COD complex **2**, the nickel may also be able to coordinate the second double bond of 1,5-COD (C. A. Tolman and W. C. Seidel, *J. Am. Chem. Soc.*, **96**, 2780 (1974)). In this connection, the relative stability of the various conformations of 1,5-COD was reported to be the following order: twist-boat>chair>boat>twist (N. L. Allinger and J. T. Sprague, *Tetrahedron*, **31**, 21 (1975)).

23) The reaction of acetylacetonato(4-cyclooctenyl)nickel with triphenyl phosphite forms Ni[P(OPh)$_3$]$_4$, 1,3-COD, and Hacac (B. Bogdanović, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966)). In view of the formation of 1,3-COD, it can be assumed that the above reaction proceeds via the isomerization of the 4-cyclooctenylnickel complex to the 3-cyclooctenylnickel complex.