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Isomerization of 1,5-Cyclooctadiene to *cis*-Bicyclo[3.3.0]oct-2-ene Catalyzed by Transition Metal Complexes

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The isomerization of 1,5-cyclooctadiene to *cis*-bicyclo[3.3.0]oct-2-ene, 1,4-cyclooctadiene and 1,3-cyclooctadiene catalyzed by transition metal complexes was studied. Nickel(II) complexes were found to have excellent catalytic activities for the isomerization to the bicyclic compound. The effect of reaction solvent, additives, reaction temperature, reaction time, catalyst concentration and 1,5-cyclooctadiene concentration were studied using $NiBr_2(PBu^n_3)_2$ as a catalyst. A modified π-allyl mechanism is proposed for the isomerization.

INTRODUCTION

It has been reported that the isomerization of 1,5-cyclooctadiene (1,5-COD) to *cis*-bicyclo[3.3.0]oct-2-ene (BCO) is catalyzed by acids (*1*), strong bases (*2*) and transition metal complexes. As for transition metal complexes, nickel tetracarbonyl in the presence of allylchloride (*3*), bicyclopentadienyl vanadium under 75 atm hydrogen (*4*) and nickel-2-ethylhexanoate in the presence of ethyldichloroaluminum or diethylchloroaluminum (*5*) have been reported to catalyze the isomerization.

We have investigated a series of catalyst systems for catalytic activity under various reaction conditions.

EXPERIMENTAL METHODS

Materials

1,5-Cyclooctadiene and 1,3-cyclooctadiene were purified by distillation over sodium. Anisole was purified by distillation over sodium and then by dehydration with molecular sieves. Other solvents were purified by distillation, and degassed on a vacuum line with a liquid nitrogen bath before use.

Preparation of Complexes

Dihalogenobis(triphenylphosphine)nickel(II) (*6*), dihalogenobis(diphenyl-*n*-butylphosphine)nickel(II) (*7*), dihalogenobis(phenyl-di-*n*-butylphosphine)nickel(II) (*7*), dihalogenobis(tri-*n*-butylphosphine)nickel(II) (*8*), dihalogenobis(tri-*p*-tolylphosphine)nickel(II) (*9*), dibromobis(triphenylphosphine)manganese(II) (*10*), dibromobis(triphenylphosphine)iron(II) (*11*), hydridotetrakis(triphenylphosphite)cobalt (I) (*12*), dibromobis(triphenylphosphine)cobalt(II) (*13*), dichlorotris(triphenylphosphine)ruthenium(II) (*14*), dihydridotetrakis(triphenylphosphine)ruthenium(II) (*15*), chlorotris(triphenylphosphine)rhodium(I) (*16*), hydridotetrakis(triphenylphosphine)rhodium(I) (*15*), chlorocarbonylbis(triphenylphosphine)rhodium(I) (*16*), dichlorobis(triphenylphosphine)palladium (II) (*17*), dichlorobis(tri-*n*-butylphosphine)palladium(II) (*18*), dichlorobis(triphenylphosphine)platinum(II) (*19*) and tetrakis(triphenylphosphine)platinum(0) (*20*) were prepared by methods reported in the literatures.

General Procedure

1,5-Cyclooctadiene (0.054 g, 0.5 mmol) and catalyst (0.025 mmol) were put into a Pyrex glass tube which had been sealed at one end. Into the mixture, solvent was added, and the total volume of the solution was made 1.0 ml. The tube was sealed under vacuum with liquid nitrogen bath. The sealed tube was heated at 180 ± 1°C for 4 hr in a silicone bath. To analyze the reaction mixture, gas–liquid chromatography was performed at 90°C with a Hitachi Perkin-Elmer instrument equipped with a flame ionization detector. A 2 m × 6 mm stainless steel column packed with 25% of 1,2,3-tris(2′-cyanoethoxy) propane on Celite 545 was used.

Isolation of the Used Complex

Dioxane was added to the mixture of $NiBr_2(PBu^n{}_2Ph)_2$ (0.133 g, 0.20 mmol) and 1,5-COD (0.054 g, 0.5 mmol), and the total volume of the solution was made 1.0 ml. The sample prepared by the method described above was heated at 180°C for 4 hr and then cooled. From the solution, volatile materials were evaporated *in vacuo*, and the residual solid was washed with alcohol and *n*-hexane, and dried *in vacuo* for 72 hr. The residual solid was identified as the original complex, $NiBr_2(PBu^n{}_2Ph)_2$, based on the following grounds; (a) elemental analysis (Calcd for $NiBr_2(PBu^n{}_2Ph)_2$: C, 50.72; H, 6.94. Found: C, 50.64; H, 6.83). (b) mp 72–73°C ($NiBr_2(PBu^n{}_2Ph)_2$: 72–73°C). (c) The infrared spectrum of the residual solid completely agreed with that of the original complex.

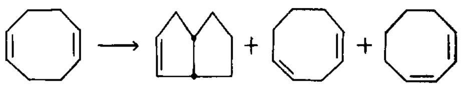
RESULTS AND DISCUSSION

Identification of cis-Bicyclo[3.3.0]oct-2-ene

BCO was identified by an authentic sample which had been prepared by the method reported in a literature (2b). The retention time of BCO in gas chromatography was identical with that of the authentic sample and different from those of cyclooctane, cyclooctene and 4-vinyl-1-cyclohexene in several columns. The cracking pattern of BCO in gas mass spectrography was identical with that of the authentic sample and with the one reported in the literature (2b).

Catalytic Activity of Phosphine Complexes

The composition of the product of the isomerization of 1,5-COD in anisole catalyzed by transition metal complexes is shown in Table 1. Though 1,4- and 1,3-cyclooctadiene (1,4-COD and 1,3-COD) were formed along with BCO in the isomerization of 1,5-COD, the rearrangement of 1,5-COD to BCO is mainly discussed in this report.



1.5-COD BCO 1.4-COD 1.3-COD

The catalytic activity of the complex of $MBr_2(PPh_3)_2$ type decreased in the order: M = Ni >> Fe ≈ Co > Mn. Though Pd(II), Rh(I) and Ru(II) complexes catalyzed well the isomerization to 1,4-COD and 1,3-COD, they hardly did the one to BCO.

The selectivity which is defined as [BCO]/([BCO] + [1,4-COD] + [1,3-COD]) × 100, was much lower in the case of Pd(II), Rh(I) and Ru(II) complexes than in the case of Ni(II) complexes. Pt(II), Pt(0) and Mn(II) complexes scarcely catalyzed any isomerization. As for phosphine ligands, the catalytic activity of the rearrangement to BCO of nickel complexes decreased in the order: $PBu^n{}_3 > PBu^n{}_2Ph > PBu^nPh_2 > P(p\text{-tolyl})_3 > PPh_3$. This order of the activity is in agreement with that of the basicity of the tertiary phosphines and shows that the electron donating nature of phosphine promotes the activity. As for halogen ligands,

TABLE 1
CATALYTIC ACTIVITY OF SOME PHOSPHINE COMPLEXES IN THE ISOMERIZATION OF 1,5-COD[a]

Catalyst	Yield of product (%) BCO	1,4-COD	1,3-COD	Selectivity[b] (%)
$NiCl_2(PPh_3)_2$	0	Tr	0	—
$\{P(p\text{-tolyl})_3\}_2$	2	2	2	33
$(PBu^nPh_2)_2$	4	3	2	44
$(PBu^n_2Ph)_2$	13	8	4	52
$(PBu^n_3)_2$	13	12	2	48
$NiBr_2(PPh_3)_2$	12	5	15	38
$\{P(p\text{-tolyl})_3\}_2$	26	9	36	37
$(PBu^nPh_2)_2$	45	10	31	52
$(PBu^n_2Ph)_2$	48	13	26	55
$(PBu^n_3)_2$	49	13	22	58
$NiI_2(PPh_3)_2$	10	8	34	19
$\{P(p\text{-tolyl})_3\}_2$	19	9	52	24
$(PBu^nPh_2)_2$	21	8	35	33
$(PBu^n_2Ph)_2$	24	10	32	36
$(PBu^n_3)_2$	26	15	33	35
$FeBr_2(PPh_3)_2$	3	5	0	38
$CoBr_2(PPh_3)_2$	2	3	0	40
$CoH\{P(OPh)_3\}_4$	0	3	66	0
$RuCl_2(PPh_3)_3$	3	0	97	3
$RuH_2(PPh_3)_4$	2	0	98	2
$RhCl(PPh_3)_3$	0	33	22	0
$RhH(PPh_3)_4$	9	15	46	13
$RhCl(CO)(PPh_3)_2$	0	16	0	0
$PdCl_2(PPh_3)_2$	1	12	85	1
$PdCl_2(PBu^n_3)_2$	0	71	10	0
$PtCl_2(PPh_3)_2$	0	0	0	—
$Pt(PPh_3)_4$	0	2	0	0
$MnBr_2(PPh_3)_2$	0	0	0	—

[a] Reaction conditions: 1,5-COD (0.5 mol liter^{-1}) and catalyst (0.025 mol liter^{-1}) were heated at 180°C for 4 hr in anisole.

[b] Selectivity is defined as [BCO]/([BCO] + [1,4-COD] + [1,3-COD]) × 100.

the activity decreased in the order: Br > I > Cl. This order of the activity results from the total action of the *trans* effect, the electronic effect and the steric effect of the halogen ligands.

Though the isomerization of 1,3-COD was examined using the five nickel bromocomplexes under the condition described in Table 1, the conversion to BCO did not exceed 6% in any case, and the isomerization to 1,4-COD and 1,5-COD was negligible. This result suggests that the direct isomerization from 1,3-COD to BCO hardly occurs.

In any case, the total amount of 1,5-COD, BCO, 1,4-COD and 1,3-COD in the reaction mixture was equal to the amount of charged 1,5-COD.

Unless otherwise noted, all the isomerizations described hereafter were carried out using $NiBr_2(PBu^n_3)_2$ as a catalyst.

Solvents

To find a suitable solvent, several compounds were examined as a solvent and the results are shown in Table 2. The isomerization proceeded well in aromatic solvents with electron donating substituents, such as *N*,*N*-dimethylaniline, aniline and anisol. However, the reaction did not occur in benzenes with electron withdrawing substituents, such as halogenated benzenes and nitrobenzene. The remarkable low selectivity of pyridine may be explained by the assumption that the solvent molecule coordinates on the reaction intermediates described below.

Dependence on Reaction Temperature

The isomerization scarcely occurred below 150°C. The conversion of 1,5-COD was 6% at 160°C, 27% at 180°C, 41% at 190°C, 79% at 200°C and almost 100% at

TABLE 2
REACTION SOLVENTS[a]

Solvent	Yield of product (%) BCO	1,4-COD	1,3-COD	Selectivity (%)
N,*N*-Dimethylaniline	60	13	25	61
Aniline	57	18	24	58
Anisole	49	13	22	58
Propionitrile	45	6	47	46
Diphenyl ether	44	14	18	58
Triethylbenzene	39	13	14	60
Dioxane	36	15	15	54
Methyl-isobutyl ketone	35	16	15	53
Pyridine	15	29	16	25
n-Hexane	14	9	6	48
Dimethylsulfoxide	10	11	3	42
o-Dichlorobenzene	0	2	0	0
Chlorobenzene	0	0	1	0
Bromobenzene	0	0	1	0
Nitrobenzene	0	0	0	—

[a] Reaction conditions: 1,5-COD (0.5 mol liter^{-1}) and $NiBr_2(PBu^n_3)_2$ (0.025 mol liter^{-1}) were heated at 180°C for 4 hr in the designated solvent.

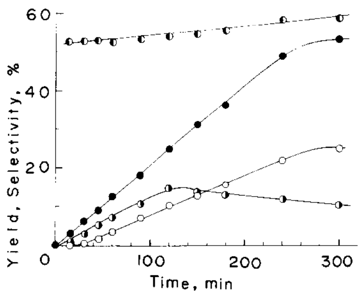


FIG. 1. The dependence of the yield and the selectivity on reaction time; NiBr$_2$(PBu$^n_3$)$_2$ (0.025 mol liter^{-1}) and 1,5-cyclooctadiene (0.5 mol liter^{-1}) were heated at 180°C in anisole: (●) BCO, (◑) 1,4-COD, (○) 1,3-COD, (◐) selectivity.

210°C in the reaction for 1 hr. The selectivity was independent of the reaction temperatures and showed nearly the same value of 55%. All other isomerization experiments were carried out at 180°C.

Dependence on Reaction Time

As shown in Fig. 1, the yield of BCO was nearly proportional to the reaction time up to 4 hr, and that of 1,4-COD showed maximum value at about 2 hr. The yield of 1,3-COD was negligible until 0.5 hr and then increased almost linearly. The absence of an induction period in the formation of BCO suggests that the bicyclic compound is formed directly from 1,5-COD. The yield vs time curve shows that the isomerization of 1,5-COD to 1,4-COD and 1,3-COD competed with that of 1,5-COD to BCO, and that of 1,3-COD to BCO hardly occurred as described before. It is inferred that the isomerization of 1,5-COD to 1,3-COD proceeded stepwisely via 1,4-COD as reported (*21*). The selectivity was independent of the reaction time. In all other cases the reaction was carried out for 4 hr.

Dependence on Catalyst Concentration

The pattern of the dependence of the product distribution and the selectivity on the catalyst concentration were similar to that on the reaction time, as shown in Fig. 2. The concentration of catalyst in all other experiments was 0.025 mol liter^{-1}.

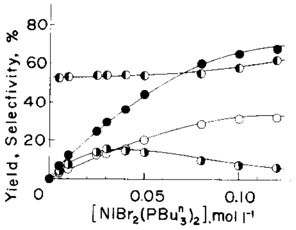


FIG. 2. The dependence of the yield and the selectivity on catalyst concentration; NiBr$_2$(PBu$^n_3$)$_2$ and 1,5-cyclooctadiene (0.5 mol liter^{-1}) were heated at 180°C for 2 hr in anisole: (●) BCO, (◑) 1,4-COD, (○) 1,3-COD, (◐) selectivity.

Dependence on the Concentration of 1,5-COD

The yield of BCO, 1,4-COD and 1,3-COD were proportional to the initial concentration of 1,5-COD below 0.7 mol liter^{-1}, respectively, and the yield of 1,4-COD and 1,3-COD were roughly a half of BCO, as shown in Fig. 3. This result suggests that only 1,5-COD molecule concerns the isomerization before rate-determining step and the coordinating power of 1,5-COD to the catalyst is not so strong at 180°C to show a leveling effect. The inference is supported by the fact that the infrared spectrum, the elemental analy-

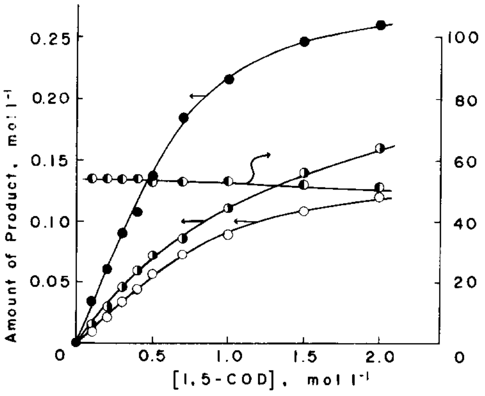


FIG. 3. The dependence of the yield and the selectivity on olefin concentration; NiBr$_2$(PBu$^n_3$)$_2$ (0.025 mol liter^{-1}) and 1,5-cyclooctadiene were heated at 180°C for 2 hr in anisole: (●) BCO, (◑) 1,4-COD, (○) 1,3-COD, (◐) selectivity.

sis and the catalytic activity of the complex, which was recovered after the isomerization, were identical with those of the original complex, $NiBr_2(PBu^n_2Ph)_2$.

Effect of Additives

The effect of several additives to the reaction system was examined and the results were shown in Table 3. The addition of PBu^n_3, $FeCl_3$, $AlCl_3$ and KOH retarded the isomerization. The retarding effect of excess PBu^n_3 is explained by the interpretation that the isomerization requires the release of one phosphine ligand from $NiBr_2(PBu^n_3)_2$, as described below. When $FeCl_3$ and $AlCl_3$ were added, especially in anisole, the total amount of eight-carbon cyclic compounds decreased. This may be caused by Friedel–Crafts reaction or acid-catalyzed polymerization. When $ZnCl_2$ was added in dioxane, both the yield of BCO and the selectivity increased and the total amount of eight-carbon cyclic compounds was equal to that of charged 1,5-COD. In the absence of $NiBr_2(PBu^n_3)_2$, $ZnCl_2$ did not catalyze the isomerization. In the case of the addition of $NaBH_4$, no isomerization was observed and 1,5-COD was hydrogenated to cyclooctene in 92% yield and to cyclooctane in 8% yield. In the absence of $NiBr_2(PBu^n_3)_2$, $NaBH_4$ did not reduce 1,5-COD. The fact that the addition of $NaBH_4$ promoted the hydrogenation rather than the isomerization, suggests that hydride complexes are not the direct precursors of the isomerization.

Nickel Bromide–Tri-n-butylphosphine System

To infer reaction intermediates, the reaction catalyzed by $NiBr_2$ and PBu^n_3 was investigated and the result is shown in Fig. 4. This figure indicates that the yield of BCO, 1,4-COD and 1,3-COD showed a maximum when the ratio of the phosphine to nickel was equal to 1.2. From the appearance of the maximum yield and the depressing effect of the added phosphine, it is inferred that 1,5-COD competes with the phosphine for a vacant coordination site on the reaction intermediate which is

TABLE 3

EFFECT OF ADDITIVES[a]

Additive	Concn (mol liter^{-1})	Solvent	Yield of product (%) BCO	1,4-COD	1,3-COD	1,5-COD	Selectivity (%)
None		Anisole	49	13	22	16	58
KOH	0.25		23	10	9	58	55
PBu^n_3	0.25		11	7	5	77	48
$NaBH_4$[b]	0.25		0	0	0	0	—
$ZnCl_2$	0.1		42	11	11	36	66
$FeCl_3$	0.1		22	7	8	15	60
$AlCl_3$	0.1		0	0	0	0	—
None		Dioxane	36	15	15	34	54
$ZnCl_2$	0.1		72	0	21	0	77
$ZnCl_2$	0.25		76	Tr	22	0	78
$ZnCl_2$[c]	0.25		0	0	0	82	—
$FeCl_3$	0.1		8	7	2	57	46
$AlCl_3$	0.1		0	0	5	27	0

[a] Reaction conditions: 1,5-COD (0.5 mol liter^{-1}), $NiBr_2(PBu^n_3)_2$ (0.025 mol liter^{-1}) and the additive of the designated concentration were heated at 180°C for 4 hr in the designated solvent.

[b] Cyclooctene (0.46 mol liter^{-1}) and cyclooctane (0.04 mol liter^{-1}) were formed.

[c] $NiBr_2(PBu^n_3)_2$ was not added.

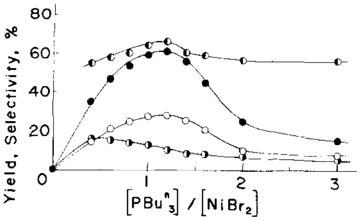
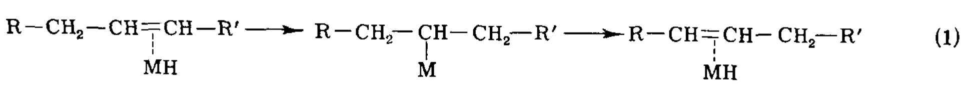


FIG. 4. The dependence of the yield and the selectivity on the ratio of PBu$^n_3$ to $NiBr_2$; $NiBr_2$(0.1 mol liter^{-1}), 1,5-cyclooctadiene (0.5 mol liter^{-1}) and PBu$^n_3$ were heated at 180°C for 4 hr in anisole: (●) BCO, (◑) 1,4-COD, (○) 1,3-COD, (◐) selectivity.

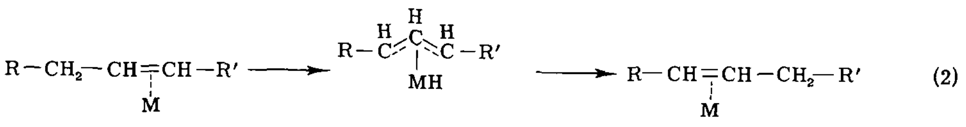
formed by the release of one tri-*n*-butylphosphine from $NiBr_2(PBu^n_3)_2$. The inference is also supported by the fact that no 1,5-COD complex was isolated even by heating the catalyst in 1,5-COD. The fact that the isomerization did not occur in the absence of PBu$^n_3$, shows that the activity of nickel complexes is not due only to their nature as Lewis acids.

GENERAL DISCUSSION

Two mechanisms have been reported for the isomerization of olefins catalyzed by transition metal complexes, that is, metal hydride addition-elimination mechanism and a π-allyl mechanism (*21*) shown in Eqs. (1) and (2), respectively.



$$R-CH_2-\underset{\vdots\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;}{\underset{MH}{CH=CH}}-R' \longrightarrow R-CH_2-\underset{M}{\underset{|}{CH}}-CH_2-R' \longrightarrow R-\underset{MH}{CH=CH}-CH_2-R' \qquad (1)$$



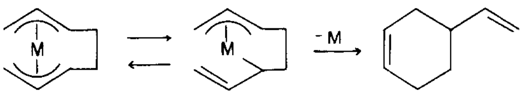
$$R-CH_2-\underset{M}{CH=CH}-R' \longrightarrow R-\overset{H\;\;\overset{H}{C}\;\;H}{C\cdots C}-R' \;\underset{MH}{} \longrightarrow R-\underset{M}{CH=CH}-CH_2-R' \qquad (2)$$

As for the double bond migration catalyzed by monohydride complexes, the former mechanism is inferred to be preferential (*22*). In our experiments, as shown in Table 1, the selectivity of Pd(II), Rh(I), Ru(II) and Co(I) complexes, which include monohydride complexes, such as $RhH(PPh_3)_4$ and $CoH\{P(OPh_3)\}_4$, were remarkably lower than that of Ni(II), Co(II) and Fe(II) complexes. This difference in selectivity must be due to such a difference in mechanism.

In the reaction catalyzed by $NiBr_2(PBu^n_3)_2$, the selectivity was hardly influenced by the reaction conditions, such as the amount of conversion of 1,5-COD, reaction time, reaction temperature, the concentration of $NiBr_2(PBu^n_3)_2$ and the concentration of PBu$^n_3$. This fact suggests that the isomerization to BCO and the migration of the double bond occurs via a common reaction intermediate. Further, the common reaction intermediate is inferred to have a tri-*n*-butylphosphine molecule, two bromide ions and a 1,5-COD molecules as ligands, on the following observations; (a) the catalytic activity showed a maximum when the ratio of the nickel to the phosphine is equal to 1.2; (b) the complex recovered after the isomerization was identical with the original complex, and the addition of sodium borohydride, which might replace a bromide ion with a hydride, showed no promoting effect; (c) the rate of the reaction showed the first order dependence on the concentration of 1,5-COD.

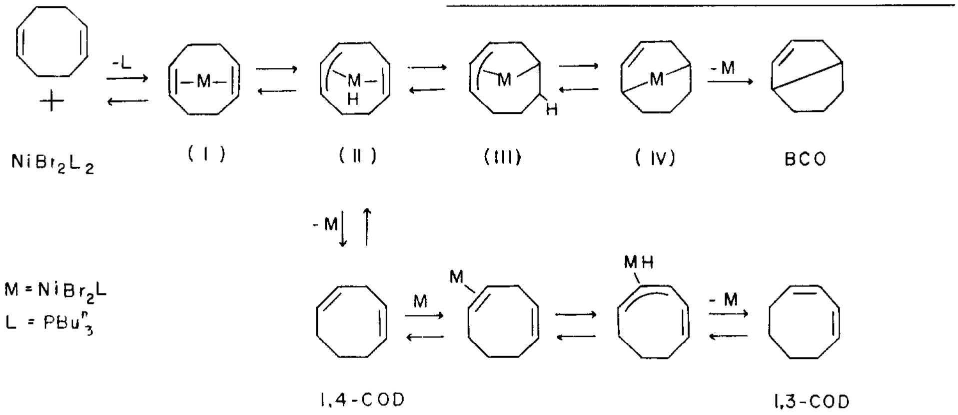
In the dimerization of butadiene to 4-vinylcyclohexene catalyzed by Ni(0) complexes, the following reaction scheme involving π-allyl-σ-alkyl intermediate, where M represents nickel atom with its auxiliary ligands, has been proposed (*23*).

Moreover, it has been recently reported



that a C–C bond is formed by the elimination of nickel atom from a π-allyl-σ-alkyl nickel complex, and that Ni(II) complexes catalyze skeletal rearrangement of 1,4-dienes (*24*).

Based on the similarity to the dimerization of butadiene and the studies concerning the migration of π-bond (*22–25*), we should like to propose the following reaction scheme.



According to this scheme, the isomerization of 1,5-COD to BCO occurs in the following sequence: (a) the release of one tri-*n*-butylphosphine from $NiBr_2(PBu^n{}_3)_2$ and the coordination of 1,5-COD to give **I**; (b) the hydrogen transfer from the coordinated 1,5-COD to the metal to yield the π-allyl hydride complex, **II**; (c) the hydrogen transfer from the metal to double bond of **II** to form the π-allyl-σ-alkyl complex, **III**; (d) the conversion of **III** to the dialkyl complex, **IV**; (e) the decomposition of **IV** to give BCO and to regenerate the catalytic active species.

As described earlier, the isomerization to BCO and that to 1,3-COD and 1,4-COD are inferred to take place via a common intermediate. In our reaction scheme, the π-allyl hydride complex, **II**, corresponds to the common intermediate and the isomerization to 1,4-COD and 1,3-COD proceeds by the π-allyl mechanism. BCO is formed directly from 1,5-COD as described previously and the rate of the isomerization of 1,4-COD to 1,3-COD has been reported to be much larger than that of the one of 1,4-COD to 1,5-COD (*26*). Therefore, the fact that the selectivity was 50–60% may denote that the rate of the isomerization of 1,5-COD to 1,4-COD is roughly equal to that of 1,5-COD to BCO.

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