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Selective Hydrogenation of 1,3-Diolefins Catalyzed by Cobalt(I)–Bipyridyl Complexes

HIROYOSHI KANAI, NOBUYUKI YAMAMOTO, KEIJI KISHI, KUNIHIKO MIZUNO, AND KIMIO TARAMA

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

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Selective hydrogenation of nonbranched 1,3-diolefins mainly to *cis*-2-olefins was carried out in THF–ethanol by the catalysis of $CoX(bpy)_2$ (X = halogen, bpy = 2,2′-bipyridyl) prepared *in situ* from cobalt halides, 2,2′-bipyridyl, and zinc. The induction period, the rate, and stereoselectivity depend on the time when 1,3-butadiene and hydrogen are introduced to the catalyst. The rate is proportional to the hydrogen pressure and to the catalyst concentration, and changes with the concentration of 1,3-butadiene. An excess of butadiene inhibits hydrogenation and leads to dimerization. A mechanism is proposed which involves an *anti*-1-methyl-π-allylcobalt complex as an intermediate.

INTRODUCTION

Selectivity according to the grade of unsaturation and stereoselectivity in the hydrogenation of conjugated dienes are keys to the character of transition metals (*1*), their oxides (*2*), and complexes (*3*). In the hydrogenation of 1,3-butadiene there are the selectivity for olefin formation and that for the formation of 1-butene or *cis*-2-butene. The selectivity for olefin formation is governed by the relative strength of adsorption (coordination) of butadiene and butene on each catalyst, and inherent activity of each catalyst for butene hydrogenation. The selective hydrogenation for olefin formation is generally achieved over transition metal complexes since butadiene coordinates competitively to a catalytic site stronger than butenes (*4*). They are divided into two groups as to whether further hydrogenation of olefins occurs or not. One is a group of catalysts which have no hydrogenation activity for olefins, $[Co(CN)_5]^{3-}$ being typically known (*5*). The other is a group of catalysts which further hydrogenate and isomerize olefins produced.

Among Co(I) complexes investigated the addition of hydrogen to conjugated dienes occurs by a 1,2-addition process over $CoX(PR_3)_3$–BF_3OEt_2 (*6*) and $[Co(bpy)(PR_3)_2]^+$ (*7*). In a preliminary account the selective hydrogenation of 1,3-butadiene to *cis*-2-butene catalyzed by Co(I)–bipyridyl complexes was reported (*8*). This paper presents the reaction scope for conjugated diene hydrogenation which outlines the selectivity according to the grade of unsaturation and stereoselectivity.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was refluxed over sodium, distilled, and stored in a nitrogen atmosphere. Methanol and ethanol were refluxed with magnesium methoxide and sodium ethoxide, respectively, and distilled. 1,3-Butadiene was obtained from Takachiho Chemical Company and distilled under vacuum. 1,3-Pentadiene and isoprene were obtained from Nakarai Chemical Company and distilled under vacuum. Other chemicals were commercial materials and used without further purification.

Cobalt Complexes

$Co(bpy)_3X$ and $Co(bpy)_2X$ (bpy = 2,2′-

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bipyridyl, X = halogen) were prepared from cobalt halides, 2,2′-bipyridyl, and zinc or sodium tetrahydroborate as a reducing agent (*9–13*). They are unstable and very sensitive to oxygen, but stable in contact with reducing agents (*10, 13*). Since large quantities of analytically pure complexes were not reproducibly obtained, we used *in situ* prepared complexes as catalysts (*14*).

Hydrogenation Procedures

Induction periods and selectivity in the hydrogenation were dependent upon the time when hydrogen and substrates were introduced to the catalyst. Three methods were examined.

Method 1. In a 100-ml flask were placed 2,2′-bipyridyl (0.88 mmol), zinc dust (4 mmol), and THF (15 ml). Ethanolic solution (5 ml) of cobalt halide (0.44 mmol) was added and the mixture was stirred at room temperature for 1 h until the color turned dark blue. After it was chilled in liquid nitrogen and degassed, 1,3-butadiene (4 mmol) was added. The flask was immersed in a bath kept at 25°C and was filled with hydrogen (580 Torr). The uptake of hydrogen started after an induction period.

Method 2. In a flask were placed 2,2′-bipyridyl (0.88 mmol), zinc (4 mmol), THF (15 ml), and ethanolic solution (5 ml) of cobalt halide (0.44 mmol). After the mixture was chilled in liquid nitrogen and degassed *in vacuo*, butadiene (4 mmol) was condensed. The flask was immersed in a bath kept at 25°C and hydrogen was introduced. The reaction mixture changed from yellow–brown to green and finally dark blue in 10–30 min. After an induction period the uptake of hydrogen started.

Method 3. After an *in situ* prepared cobalt complex was treated with butadiene at 0°C for 2 h, the reaction mixture was warmed to 25°C and was filled with hydrogen. The uptake of hydrogen was observed without an induction period.

The course of the hydrogenation with time was followed by the uptake of hydrogen and intermittent sampling of the reaction mixture and analyzing with a Hitachi-063 and a Shimadzu-GC3BF gas chromatograph (30% dimethylsulfolane/C-22, 5 m, 5.6 m, r.t.) equipped with FID. The deuterated products were analyzed by ^1H and ^{13}C NMR spectra obtained with a JEOL-PM60 and a JEOL-FX100 spectrometers.

Dimerization of 1,3-Butadiene

In a 40-ml ampoule were placed cobalt halide (0.5 mmol), 2,2′-bipyridyl (n_1 mmol), zinc (5 mmol), THF (10 ml), and ethanol (n_2 ml). After degassing 1,3-butadiene (26 mmol) was condensed and the ampoule was sealed. The ampoule was stirred at r.t. for 5 days. The products were analyzed with a Shimadzu-6A gas chromatograph (20% silicon SE-30/Celite 545, 3 m, 80°C) equipped with FID. Each product was isolated with a preparative gas chromatograph and identified by ^1H and ^{13}C NMR spectra.

RESULTS

Activation of Hydrogen

No hydrogen absorption was observed with *in situ* prepared Co(I)–bipyridyl complexes. In contrast to the formation of $[Co(H_2)(bpy)(PR_3)_2]^+$ (PR_3 = PEt_3, PPr_3, PBu_3, $PPhEt_2$) (*7*) no formation of cobalt–hydride complexes occurs from an atmospheric hydrogen alone. When 1,3-butadi-

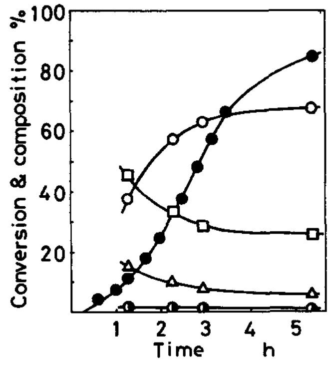


FIG. 1. Hydrogenation of 1,3-butadiene catalyzed by *in situ* prepared $CoBr(bpy)_2$ at 25°C (method 1): ●, conversion; □, $1\text{-}C_4H_8$; ○, *cis*-$2\text{-}C_4H_8$; △, *trans*-$2\text{-}C_4H_8$; ◑, *n*-C_4H_{10}.

TABLE 1

Hydrogenation of 1,3-Butadiene Catalyzed by *in situ* Prepared CoX(bpy)$_2$[a]

X	Induction period (min)	Rate of H_2 uptake (ml/min)	Composition of butenes[b] (%)		
			1-	*trans*-2-	*cis*-2-
Cl[c]	4	0.33	53	18	27
Br[c]	12	0.48	33	9	57
I[c]	40	0.69	21	3	77
Cl[d]	60	0.48	17	3	80
Br[d]	75	0.56	17	2	81
I[d]	19	1.29	17	2	81

[a] Complexes were prepared *in situ* from CoX_2 (0.44 mmol), 2,2′-bipyridyl (0.88 mmol), and zinc (4 mmol) in THF (15 ml) and ethanol (5 ml). 1,3-C_4H_6 (4 mmol), P_{H_2} 580 Torr., 25°C.

[b] At 32–43% conversions.

[c] Method 1.

[d] Method 2.

TABLE 2

Effects of the Ratio of 2,2′-Bipyridyl to Cobalt in the Hydrogenation of 1,3-Butadiene by *in situ* Prepared Co(I) Complexes (Method 2)[a]

bpy/Co	Induction period (min)	Rate of H_2 uptake (ml/min)	Composition of butenes (%)		
			1-	*trans*-2-	*cis*-2-
1.0	50	0.66	19	2	79
1.5	65	1.10	17	2	81
2.1	19	1.29	17	2	81
2.5	70	0.50	20	2	78
3.1	60	0.28	17	3	80

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

ene was added, hydrogen uptake took place after an induction period (Fig. 1). The composition of butenes produced in method 1 changed with the lapse of time: in the bromo complex system 1-butene was initially formed mainly but afterward *cis*-2-butene exceeded it. The induction periods, the rates of hydrogenation, and the composition of butenes are dependent upon halides as shown in Table 1.

When Co(I) complexes were prepared in the presence of 1,3-butadiene and hydrogen (method 2), the induction period in the iodo complex system decreased. One of characteristics in method 2 is that high selectivity for the formation of *cis*-2-butene remains unchanged during the reaction and is independent of halides (Fig. 2, Table 1). The rates of hydrogenation are higher than those in method 1 and decrease in the order I > Br > Cl similarly with the hydrogenation in method 1 (Table 1).

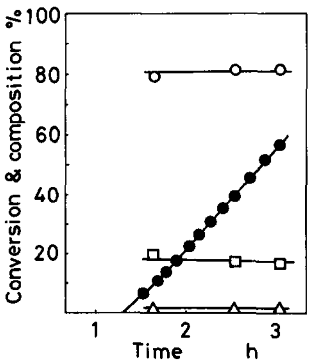


FIG. 2. Hydrogenation of 1,3-butadiene catalyzed by *in situ* prepared Cobr(bpy)$_2$ (method 2): symbols are the same as those in Fig. 1.

In method 3 cobalt complexes were reduced in the presence of 1,3-butadiene. When the catalyst solution was supplied into an H_2 atmosphere, constant uptake of hydrogen was observed without an induction period. As described in the Experimental section, we could not get pure Co(bpy)$_2$X. The filtrate of *in situ* generated Co(I) complexes gave no catalytic activity for hydrogenation but showed catalysis for 1,3-butadiene hydrogenation by the addition of zinc. Catalytic species for selective formation of *cis*-2-butene are presumably produced *via* the reaction of Co(I)–bipyridyl complexes and 1,3-butadiene in THF–ethanol in the presence of zinc.

Effects of the Ratio of Bipyridyl to Cobalt

The effects of the ratio of bipyridyl to cobalt were examined according to method 2 (Table 2). The maximum rate was ob-

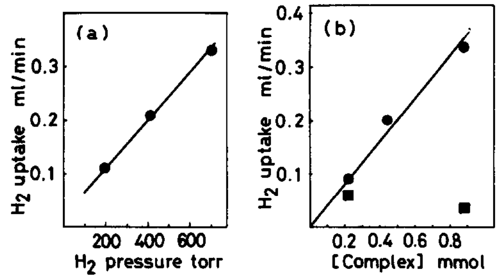


FIG. 3. Dependence of (a) hydrogen pressure and (b) catalyst concentration (●, 1,3-C_4H_6 4 mmol; ■, 1,3-C_4H_6/Co = 10) on the rate of hydrogenation of 1,3-butadiene at 0°C (method 3).

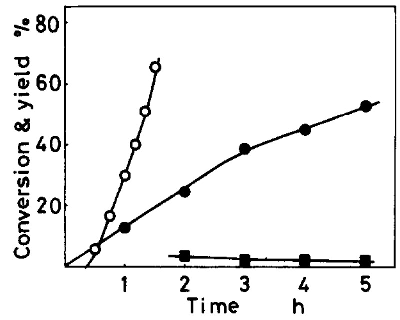


FIG. 5. Plots of 1,3-butadiene conversion vs time: ○, conversion in H_2; ●, conversion in N_2; ■, yield of total butenes in N_2.

served at bpy/Co = 2, where the induction period was the shortest. However, no correlation has yet been established between the induction period and the rate of hydrogenation. The composition of butenes remains unchanged irrespective of any ratios of bipyridyl to cobalt. The precursor of catalytic species is presumed to be $Co(bpy)_2X$.

Effects of Hydrogen Pressure, the Concentration of Cobalt Complexes and 1,3-Butadiene, and Solvent Effect

The effects of reaction conditions were examined at 0°C according to method 3, where no induction period was observed and the rates of hydrogenation were the same as those according to method 2.

The hydrogenation is of the first order with hydrogen pressure as shown in Fig. 3a. The effect of the concentration of a cobalt complex is complicated (Fig. 3b). At a constant concentration of butadiene the rate increases in proportion to the concentration of a cobalt complex. However, at a constant ratio of butadiene to a cobalt complex there is no relationship between the rate and the concentration of the complex. Complicating features may be due to the absolute concentration of butadiene in the reaction. A large excess of butadiene inhibits the hydrogenation as shown in Fig. 4 (*15*). Butadiene was consumed in the absence of hydrogen (Fig. 5) and products were dimers and hydrodimers (*vide post*) and a small amount of butenes (1-C_4H_8, 53%; *c*-2-C_4H_8, 31%; *t*-2-C_4H_8, 16%) whose composition is different from that in the presence of hydrogen. Hydrogen and butadiene coordinate competitively toward a Co(I)–butadiene complex: the former leads to hydrogenation and the latter to dimeriza-

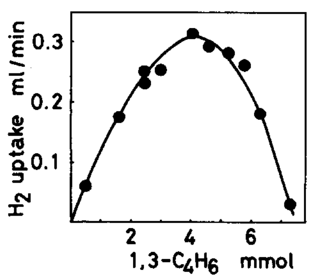


FIG. 4. Effect of 1,3-butadiene concentration on the rate of hydrogenation of 1,3-butadiene at 0°C (method 3).

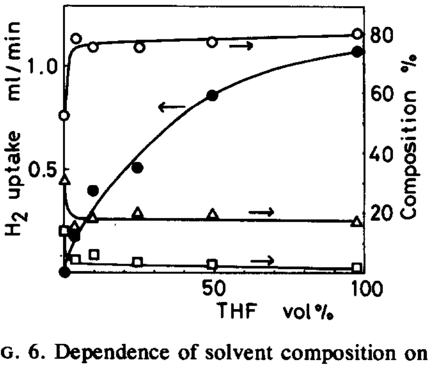


FIG. 6. Dependence of solvent composition on the rate of hydrogenation of 1,3-butadiene in THF–ethanol at 20°C: ●, H_2 uptake; △, 1-C_4H_8; ○, *cis*-2-C_4H_8; □, *trans*-2-C_4H_8.

TABLE 3

Hydrogenation of Conjugated Dienes and Olefins[a]

Substrate	Rate of H_2 uptake (ml/min)	Conv. % (h)	Product distribution		
1,3-Butadiene	1.29	36 (1)	1-C_4H_8 17	*trans*-2-C_4H_8 2	*cis*-2-C_4H_8 81
1,3-Pentadiene	0.13	37 (5)	1-C_5H_{10} 5	*trans*-2-C_5H_{10} 11	*cis*-2-C_5H_{10} 84
Isoprene	—	13 (5)	2-Methyl-1-butene 50	2-Methyl-2-butene 38	3-Methyl-1-butene 12
Styrene	—	10(22)	Ethylbenzene 100		
1-Butene	—	6(22)	*n*-C_4H_{10} 33	*trans*-2-C_4H_8 43	*cis*-2-C_4H_8 24

[a] Complexes were prepared in a similar manner as those in Table 1. Substrate (4 mmol), method 2.

tion. Thus, the excess of butadiene blocks the coordination of hydrogen.

Alcohols are required to produce Co(I)–bipyridyl complexes from the reduction of Co(II) complexes by zinc. The rate increases with the amount of THF (Fig. 6). No hydrogen uptake was observed in ethanol alone, but butenes were formed with the composition different from that in THF–ethanol. So long as THF is added, hydrogen uptake results in the selective formation of *cis*-2-butene. The rate was approximately doubled when water was added in 4 vol%, however, the excess was ineffective. The addition of water results in lowering the selectivity for *cis*-2-butene (76%).

The rate of hydrogenation of 1,3-butadiene catalyzed by *in situ* prepared CoI$(phen)_2$ (phen = *o*-phenanthroline) was equal to one-third the rate catalyzed by CoI$(bpy)_2$. There was no difference in butene composition between them.

Hydrogenation of Other Dienes and Olefins

Conjugated dienes without branching are readily hydrogenated. Hydrogen uptake was scarcely observed for reactions of conjugated dienes with branching and simple olefins (Table 3), but hydrogenated products were produced in small amounts. *cis* Selectivity is maintained in the hydrogenation of 1,3-pentadiene. However, no stereoselectivity was observed in the hydrogenation of isoprene.

Dimerization of 1,3-Butadiene

Dimerization of 1,3-butadiene was catalyzed by Co(I)–bipyridyl complexes in the absence of hydrogen (Fig. 7). Products are classified into dimers, 3-methyl-1,4,6-heptatriene, **1**, *trans,trans*-1,3,6-octatriene, **2**, and *trans,cis*-1,3,6-octatriene, **3**, and hydrodimers, 3-methyl-1,5-heptadiene, **4**, and 2,6-octadiene, **5** (Table 4). Among the various types of oligomerization of butadiene

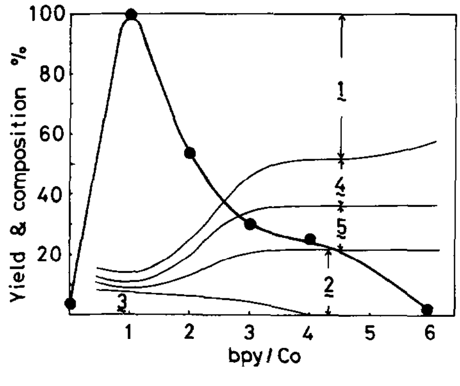
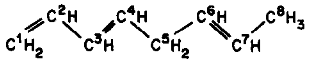
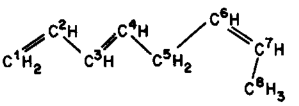
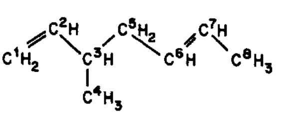
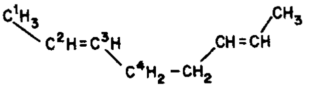


FIG. 7. Dimerization of 1,3-butadiene catalyzed by *in situ* prepared CoI$(bpy)_n$: ●, yield.

TABLE 4

Characterization of Products

Product	δ ^{1}H NMR	ppm (CDCl$_3$) (^{13}C NMR)
 2		17.89 (C^8) 35.51 (C^5) 115.04 (C^1) 126.15 (C^7) 128.69 (C^6) 131.26 (C^4) 133.40 (C^3) 137.07 (C^2)
 3		12.71 (C^8) 29.94 (C^5) 115.00 (C^1) 125.06 (C^7) 127.40 (C^6) 131.03 (C^4) 133.05 (C^3) 137.11 (C^2)
 4	0.98 (3H, d, J = 5.6 Hz) 1.65 (3H, m) 1.7–2.5 (3H, m) 4.8–5.0 (2H, m) 5.3–5.9 (3H, m)	17.89 (C^8) 19.38 (C^4) 37.74 (C^5) 39.76 (C^3) 112.23 (C^1) 126.15 (C^7) 129.43 (C^6) 144.35 (C^2)
 5	1.5–1.8 (6H, m) 2.05 (4H, bs) 5.3–5.7 (4H, m)	17.93 (C^1) 32.71 (C^4) 124.86 (C^2) 130.94 (C^3)

investigated (*17, 18*) linear dimerization of butadiene leads mainly to 1 with a small amount of 2 by cobalt complexes, CoCl$_2$–AlEt$_3$ (*19*), Co$_2$(CO)$_8$–AlEt$_3$ (*20, 21*), Co(acac)$_3$–AlEt$_3$ (*22, 23*), and CoEt$_2$(bpy)$_2$ (*24*). The formation of **1** occurs from hydrogen transfer at 1- and 4-position of butadiene *via* a Co(butadiene)(1,3-π-5-methylheptadienyl) intermediate (*25*). However, cyclodimerization gave 1,5-cyclooctadiene and 4-vinyl-1-cyclohexene in preference to linear dimers in the CoX(PPh$_3$)$_3$ (X = Cl, Br) system (*26*).

A maximal conversion was obtained at bpy/Co = 1 while the most suitable molar ratio of bipyridyl to cobalt in the hydrogenation is 2. Dimerization requires one more

TABLE 5

Dimerization of 1,3-Butadiene Catalyzed by *in situ* Prepared CoX(bpy)$_n$^{a}

n	X	Total yield (%)	Products					Linear dimers (%)	Hydrodimers
			1	2	3	4	5		
1	Cl	50	90.0	0.6	7.9	0.8	0.7	9.2	1.5
1	I	100	88.5	1.4	7.3	1.5	1.3	10.0	2.8
2	Cl	10	74.1	4.7	9.2	5.6	6.4	20.3	12.0
2	Br	22	83.5	2.5	8.7	2.9	2.4	13.6	5.3
2	I	53	74.7	7.7	6.8	5.0	5.8	20.3	10.8

[a] Co(I) complexes were prepared *in situ* from CoX$_2$ (0.5 mmol), 2,2′-bipyridyl, and Zn (5 mmol) in THF (10 ml) and ethanol (2 ml). 1,3-C$_4$H$_6$ (26 mmol), r.t., 5 days.

vacant site for coordination of butadiene than hydrogenation does. As the ratio of bpy/Co is increased over 1, the composition of linear and diene dimers increases and it remains unchanged at bpy/Co > 3 where the formation of **3** ceases. With increasing the amount of ethanol the conversion once decreased and then increased. The composition of products remains almost unchanged in any composition of ethanol. The conversion decreases in the order I > Br > Cl which is in accord with that of hydrogenation (Table 5). The difference in the composition of products between halide systems is hardly discernible.

Deuteration of 1,3-Butadiene

Deuterated products of 1,3-butadiene hydrogenation were analyzed by ^{1}H and ^{13}C NMR (Fig. 8). The methyl group of *cis*-2-butene consists of CH_2D and CH_3 (molar ratio 79:21). Most of 1-butene is $CH_2{=}CHCHDCH_3$ and a small part of CH_2 group is observed, but the deuterated methyl group is hardly discernible. Olefinic hydrogens in all butenes and 1,3-butadiene were not deuterated at all.

DISCUSSION

Hydrogen uptake occurred after induction periods when Co(I)–bipyridyl complexes were applied to 1,3-butadiene and hydrogen. The induction periods were shortened in method 3, where Co(I) complexes were previously reacted with butadiene in THF–ethanol followed by exposure to hydrogen. The consumption of butadiene starts before the hydrogen uptake (Fig. 5). There is no induction period in the hydrogenation catalyzed by Co(I)–bipyridyl complexes prepared *in situ* from the reduction by $NaBH_4$, where the composition of butenes is 1-C_4H_8, 21.2%; *cis*-2-C_4H_8, 72.2%; and *trans*-2-C_4H_8, 6.6% somewhat different from that in the hydrogenation by Co(I) complexes prepared from the reduction by zinc. A disadvantage in the $NaBH_4$ system is a gradual decrease of catalytic activity with the lapse of time. The roles of $NaBH_4$ are thought to be a reductant as well as a reagent for producing cobalt–hydride complexes. In the absence of bipyridyl, hydrogenation of butadiene occurred with CoX_2–Zn or $NaBH_4$ systems in which neither

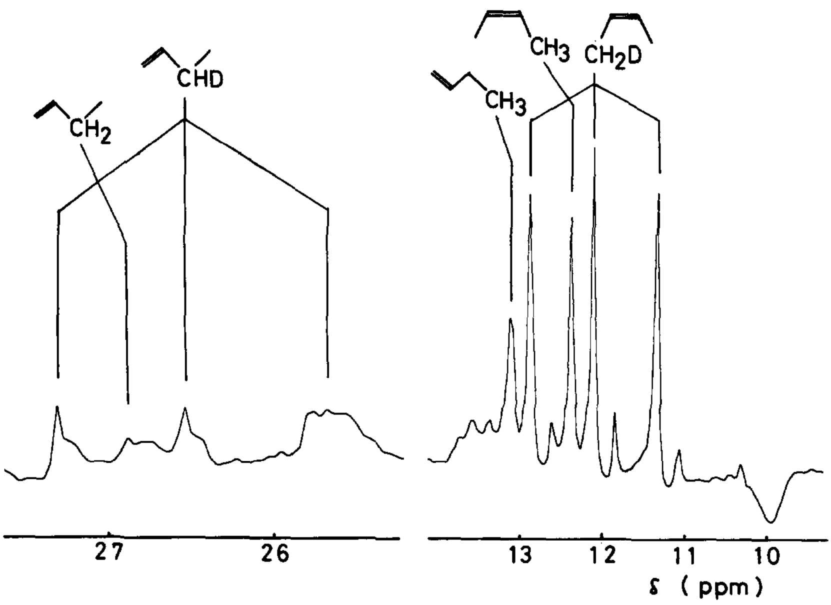


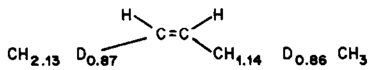
FIG. 8. ^{13}C NMR spectrum of deuterated butenes.

selectivity according to the grade of unsaturation nor stereoselectivity was observed. Thus, the induction period is explained to be required for the formation of catalytic species from Co(I)–bipyridyl complexes and conjugated dienes in the presence of zinc.

The hydrogenation of conjugated dienes catalyzed by Co(I)–bipyridyl complexes gives mainly *cis*-2-olefins, while CoBr $(PPh_3)_3$–BF_3OEt_2 (*6*) catalyzes similar reaction to give terminal olefins as the main products. In addition to the selectivity in products there are differences in specificity of substrates and dependence of rates on the substrate concentration. Another characteristic feature is that the former complexes have no activity for isomerization and dimerization of simple olefins, while the latter complex does.

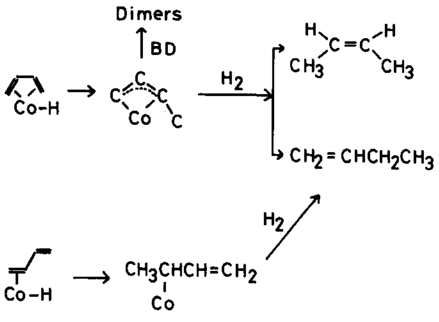
Chromium carbonyl complexes prepared from photolysis of $Cr(CO)_6$ or substituted by aromatic or acetonitrile compounds catalyzed the 1,4-addition of hydrogen to conjugated dienes (*27–30*). The requisite for selectivity is cisoid coordination of conjugated dienes. 1,4-Hydrogen addition is predominantly molecular since monoene-d_2 is the main product in D_2, and it is a mixture of monoene-d_0 and monoene-d_2 with H_2–D_2.

The hydrogenation of conjugated dienes by Co(I)–bipyridyl complexes occurs in a manner somewhat different from that of those by $CoBr(PPh_3)_3$–BF_3OEt_2 and chromium carbonyl complexes. In the deuteration of 1,3-butadiene *cis*-2-butene-d_2 is contaminated slightly with *cis*-2-butene-d_1 and -d_0. The deuteration of 1,3-pentadiene gave



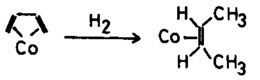
by analysis of its ^{13}C NMR spectrum. The contamination of hydrogen at 1,4-position accounts for the induction period in which catalytic species are formed from Co(I) complexes and dienes in THF–ethanol independent of the hydrogen atmosphere.

Methyl vinyl ketone was hydrodimerized to 2,7-octanedione by Co(I)–bipyridyl complexes in protic solvents (*13*). The reaction between Co(I) complexes and 1,3-butadiene in a protic solvent may give 1-methyl-π-allylcobalt complexes *via* the protonation of cobalt–butadiene π complexes. In the absence of hydrogen butadiene adds to 1-methyl-π-allylcobalt complexes to give dimers, while hydrogen adds competitively to those complexes to give butenes.



(1)

(2)



(3)

The structure of 1-methyl-π-allylcobalt complex is thought to be *anti* rather than *syn*. *anti*-1-Methyl-π-allylcobalt tricarbonyl is reacted with cobalt hydride to give 1-butene, 35% and *cis*-2-butene, 65%, while the *syn* isomer gives 1-butene, 8%, *trans*-2-butene, 86%, and *cis*-2-butene, 6% (*32*).

In method 1 the initial products are rich in 1-butene, which accounts for that butadiene first coordinates in a fashion of 1,2-olefinic bond (Eq. (2)). This coordination prolongs in the chloro complex system more than that in the iodo complex system. As time elapses, the coordination moves from 1,2-bond to cisoid structure giving selectively *cis*-2-butene. When there is plenty of time for 1,3-butadiene to coordinate to cobalt in a manner of cisoid structure, *cis*-2-butene is selectively produced from the beginning. Since the selectivity for *cis*-2-olefins is high, simultaneous 1,4-addition of hydrogen in a similar manner as that in chromium carbonyl systems cannot be denied (Eq. (3)).

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14. As soon as $Co(bpy)_2X$ (X = halogen) dried up during isolation, the complexes decomposed with color change from dark blue to yellow–brown. We could not get them except $Co(bpy)_2ClO_4$ which was inactive for hydrogenation of 1,3-butadiene.

15. Analogous phenomena of self-inhibition were observed in the heterogeneous hydrogenation of acetylenes (*16*), where the order in which hydrogen and acetylene are introduced to the catalyst affects the course of hydrogenation.

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