16 © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 16—22 (1985) [Vol. 58, No. 1

Selective Hydrogenation of Conjugated Dienes Catalyzed by Thiocyanatotris(triphenylphosphine)cobalt(I)

Taisei NAKAYAMA and Hiroyoshi KANAI*
Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received June 7, 1984)

Thiocyanatotris(triphenylphosphine)cobalt(I) prepared *in situ* from bis(thiocyanato)bis(triphenylphosphine)cobalt(II), triphenylphosphine, zinc bromide, selectively hydrogenated conjugated dienes to the corresponding cis-monomenes. The C_2-or/and C_3-methyl substituted 1,3-butadienes enhance the reactivity by a factor of 2.3 per one methyl group, while C_1- or/and C_4-methyl substituted 1,3-butadienes lower the reactivity by a factor of 1/23 per one methyl group. In the hydrogenation of cyclic conjugated dienes α-angle ($\angle$C–C=C) is closely related to the hydrogenation rate. The rates of hydrogenation in cyclic ethers are greater than those in acyclic ethers, but the cis-selectivity in acyclic ethers is much higher. Deuterium selectively adds to 1,3-butadiene and 2,5-norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) to give 3,4-dideuterio-1-butene and *cis*-1,4-dideuterio-2-butene, and *endo,endo*-5,6-dideuterionorbornene and *endo,endo*-3,5-dideuterionortricyclene, respectively. A mechanism is proposed which derives from *anti*-π-allylcobalt hydride or delocalized nortricyclenylcobalt hydride as an intermediate.

Univalent cobalt complexes with halogen and pseudohalogen ligands were limited until recently.[1] The principal difficulties in the synthesis of Co(I) complexes are due to the capacity of Co(I) complexes for oxidation, reduction and disproportionation. The interest in Co(I) complex has been stimulated by studies in the field of stereochemistry[2] and catalysis.[3]

In the hydrogenation of 1,3-butadiene a cationic cobalt(I) complex, $[Co(PPh_3)_3]BF_3X$ (X=halogen),[3d] selectively gave 1-butene, while $CoX(bpy)_2$/zinc system (bpy=2,2′-bipyridyl) mainly gave *cis*-2-butene.[3h]

We reported here the selective hydrogenation of conjugated dienes with a cobalt(I) thiocyanate complex.

Experimental

Materials. 1,3-Butadiene was obtained from Takachiho Chemical Co. and distilled under vacuum. *trans*-1,3-Pentadiene, *trans*-2-methyl-1,3-pentadiene, *trans,trans*-2,4-hexadiene, 4-methyl-1,3-pentadiene and 2,3-dimethyl-1,3-butadiene were obtained from Aldrich Chemical Co. and distilled under vacuum. Isoprene and 1,3-cyclohexadiene were from Nakarai Chemical Co. and distilled under vacuum. Cyclopentadiene was prepared from the pyrolysis of dicyclopentadiene.[4] 1,3,5-Cycloheptatriene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, β-myrcene and 2,5-norbornadiene were obtained from Nakarai Chemical Co. and used without further purification. 1,2-Butadiene was obtained from Tokyo Kasei Co. and distilled under vacuum.

Solvents were refluxed over lithium aluminium tetrahydride, distilled, and stored in a nitrogen atmosphere.

Preparation of Bis(thiocyanato)bis(triphenylphosphine)cobalt(II).[5] Cobalt(II) thiocyanate was prepared from cobalt(II) sulfate (Hayashi Junyaku Co.) and barium thiocyanate (Mitsuwa Kagaku Co.) by the literature method.[6] After $Co(SCN)_2$ (28 g, 98 mmol) was dissolved in acetone (300 ml) and the insoluble residue was filtered off, triphenylphosphine (48 g, 200 mmol) were added to the filtrate and the green solution was concentrated to *ca.* 100 ml by using an evaporator. Petroleum ether was added to the concentrated solution. The precipitate of $[Co(SCN)_2(PPh_3)_2]$ was collected, washed with petroleum ether for several times and dried: yield 32 g (67% based on $Co(SCN)_2$).

Hydrogenation Procedure. The catalyst was prepared *in situ* from the reduction of $[Co(SCN)_2(PPh_3)_2]$ 0.21 g (0.3 mmol) with Zn (3.0 mmol) and $ZnBr_2$ (1.0 mmol) in the presence of PPh_3 (0.3 mmol) in glyme (1,2-dimethoxyethane) (10 ml) under nitrogen. The solution, which was initially purple, turned brown after 2—3 h. Then substrates (2 mmol) were added and nitrogen was replaced by hydrogen. Hydrogenation was conducted at 17 °C with stirring under the constant pressure of hydrogen using the gas buret. The rate of hydrogenation was determined by hydrogen uptake and products were analyzed by gas chromatography (30% 2,4-dimethylsulfolane on C-22, 5.6 m, r.t.).

Isotopic exchange of H_2–D_2 and D_2–olefin were carried out by the analogous procedure. The deuterated products of 1,3-butadiene in H_2–D_2 mixed gas were analyzed by a gas chromatography–mass spectrometer (NEVA TE600, porapak Q, 110 °C, ionization voltage 10 V). Deuterated products of 1,3-butadiene and 2,5-norbornadiene were identified by ^{13}C and ^1H NMR spectra obtained on a JEOL FX-100 spectrometer.

Results and Discussion

Preparation of Co(I) Complex and Active Species. Sodium tetrahydroborate was ineffective to decompose the complex. Zinc can reduce $[Co(SCN)_2(PPh_3)_2]$ to the Co(I) complex, but it takes too much time. The activated zinc prepared from zinc halides and potassium,[7] or from zinc bromide, lithium and naphthalene[8] was not appropriate because they gave complexed compounds to lose reproducibility. We found that $[Co(SCN)_2(PPh_3)_2]$ was smoothly reduced by zinc in the presence of zinc bromide.[9] The effect of zinc bromide on the hydrogenation of 1,3-butadiene indicates that the highest activity was observed above the ratio of $ZnBr_2/Co=3.3$ (Fig. 1). Other Lewis acids, $AlCl_3$ and $FeCl_3$ were ineffective. Zinc bromide was the most effective among zinc halides.

The addition of triphenylphosphine increased the

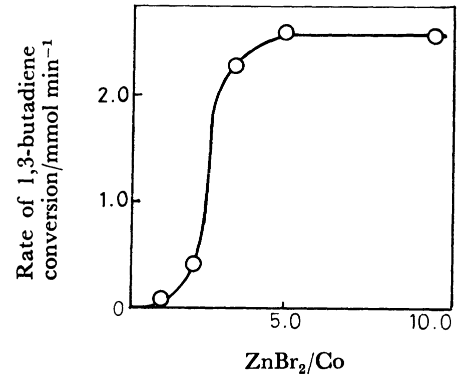


Fig. 1. Effect of zinc bromide on the hydrogenation of 1,3-butadiene.

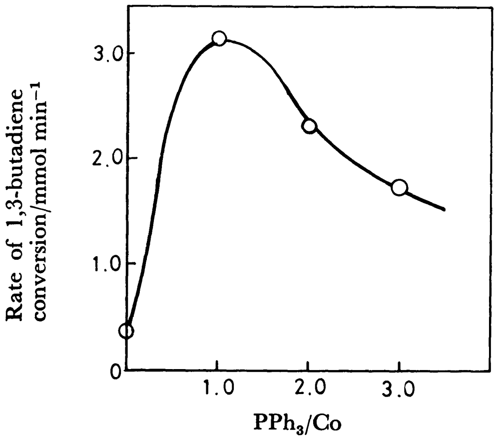
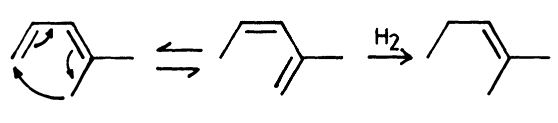


Fig. 2. Effect of triphenylphosphine on the hydrogenation of 1,3-butadiene.

yield of hydrogenation, but the excess inhibited (Fig. 2). The maximum yield at the 1 : 1 ratio of triphenylphosphine to the cobalt complex indicated that the precursor of the active species is [Co(SCN)(PPh$_3$)$_3$]. After the reduction of [Co(SCN)$_2$(PPh$_3$)$_2$] in the presence of PPh$_3$, ZnBr$_2$, and Zn, the red-brown solution was separated from zinc by filtration. When 1,3-butadiene was introduced into the filtrate in an atmosphere of hydrogen, no reaction was observed. When butadiene was treated with another filtrate in contact with fresh zinc, hydrogenation began to occur. Zinc plays a role to keep the cobalt complex a univalent state. No anion exchange between [CoBr(PPh$_3$)$_3$] and NaSCN was observed in glyme at r.t. The red-brown solution where [CoBr(PPh$_3$)$_3$] was treated with Zn(SCN)$_2$ caused hydrogenation of 1,3-butadiene, but hydrogen uptake stopped after 60 min by giving catalytically inactive green complex. Consequently, anion exchange method was not suitable to prepare the Co(I) complex.



Scheme 1.

We have not isolated the Co(I)-thiocyanate complex. Putting all accounts together catalytic species must be [Co(SCN)(PPh$_3$)$_3$]. The presence of zinc is required as a reductant to keep the unstable complex active.

Hydrogenation of Unsaturated Hydrocarbons. Hydrogenation of unsaturated compounds were summarized in Table 1. Conjugated acyclic dienes were selectively hydrogenated to the corresponding cis-monoenes. No alkanes were observed. The rates of hydrogenation decreased in the following order; 2,3-dimethyl-1,3-butadiene>*trans*-2-methyl-1,3-butadiene-(Isoprene)>1,3-butadiene>*trans*-2-methyl-1,3-pentadiene>*trans*-1,3-pentadiene. *trans,trans*-2,4-Hexadiene was not hydrogenated. 4-Methyl-1,3-pentadiene was concluded to be hydroganated *via* 2-methyl-1,3-pentadiene, since hydrogenation products were the same as those of 2-methyl-1,3-pentadiene which had been formed in the course of hydrogenation. This reaction is similar to the 1,5-hydrogen shift explained by Frankel and Butterfield (Scheme 1).[10]

To investigate the coordination and reactivity sequences of conjugated dienes, the competitive hydrogenation of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene was conducted. Since the hydrogenation of each dienes occurred at its own rate, the coordinating strength of dienes did not determine the reactivity sequence.

Among conjugated cyclic dienes, cyclopentadiene and 1,3-cyclohexadiene were selectively hydrogenated to the corresponding cyclomonoenes. 1,3,5-Cycloheptatriene was also hydrogenated to cycloheptene *via* 1,3- or 1,4-cycloheptadiene. No hydrogenation of 1,3- and 1,5-cyclooctadiene occurred. 1,5-Cyclooctadiene was isomerized to 1,3- and 1,4-cyclooctadienes. The composition of cyclooctadienes after 24 h were 1,3-cyclooctadiene : 1,4-cyclooctadiene : 1,5-cyclooctadiene= 4 : 29 : 67. 1,2-Butadiene was hydrogenated to butenes without selectivity but polymer was obtained as a by-product.

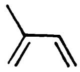
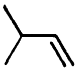
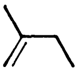
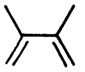
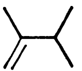
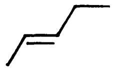
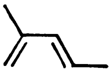
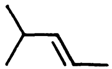
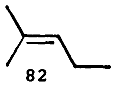
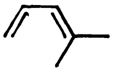
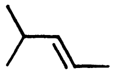
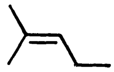
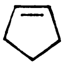
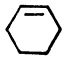
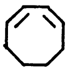
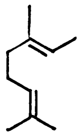
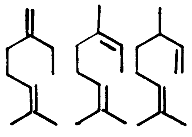
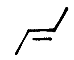
Although 2,5-norbornadiene is classified as a non-conjugated diene, Hoffmann *et al.* showed that its π-electron systems have direct through-space overlap interaction.[11] So it should be treated as one of conjugated dienes when it is coordinated to cobalt complex.

2,5-Norbornadiene was hydroganeted to bicyclo-[2.2.1]hept-2-ene (norbornene) and tricyclo[2.2.1.0^{2,5}]-heptane (nortricyclene). It is notable that nortricyclene is produced in the hydrogenation of norbornadiene by a cobalt catalyst, while it is barely produced by transition-metal complexes.[12] Parallel to the hydrogenation, dimerization occurred.[13] No dimerization of any other conjugated dienes in Table 1 was observed.

No hydrogenation occurred for following unsaturated compounds; 1-hexyne, styrene, *trans*-1-phenyl-1,3-butadiene, phenylacetylene, furan, and methyl acrylate.

Effect of Hydrogen Pressure, and the Concentrations of

TABLE 1. HYDROGENATION OF CONJUGATED DIENES CATALYZED BY $[Co(SCN)(PPh_3)_3]$ PREPARED *in situ* FROM $[Co(SCN)_2(PPh_3)_2]$, Zn AND $ZnBr_2$[a)]

Diene	Rate of H_2 uptake 10^{-2} ml min^{-1}	Products %
	10	 18  0  82
	23	 11  1  88
	50	 3  97
	0.40	 28  6  66
	2.0	 13  5  82
	0.33	 13  14  73
	0	
	21	 100
	10	 100
	0.06	 100
	0	
	17[b)]	 75  25
C=C=C-C	9.0	 38  14  48 + Polymer
	3.0	 55  48 55 + 48 = 68 + Dimers 32

a) Reactions were carried out as following conditions: diene 2 mmol, $[Co(SCN)_2(PPh_3)_2]$ 0.3 mmol, Zn 3.0 mmol, $ZnBr_2$ 1.0 mmol, glyme 10 ml, total pressure 1 atm at 17 °C.
b) β-Myrcene (1.2 mmol) was used.

Cobalt Complex and Dienes. Figure 3 illustrates the first order dependence upon hydrogen pressure. The first order dependence upon the concentration of the complex is observed up to a cobalt complex charge of 0.03 mol dm^{-3} which is the saturated concentration (Fig. 4). The hydrogenation is independent of the concentration of dienes except for β-myrcene. The lowering of the rate in the hydrogenation of β-myrcene with the elapse of time is attributed to the coordination of the diene products. Hydrogen uptake increases linearly with time, and products were not isomerized until dienes were almost consumed.

Solvent Effects. The nature of solvents has a significant effect on both the selectivity and the hydrogenation rate (Table 2). No reduction of [Co(SCN)$_2$(PPh$_3$)$_2$] occurred in the following solvents; diethyl ether, dibutyl ether, and toluene. Methanol, ethanol, and acetonitrile were inadequate to make the complex dissociate into Co(SCN)$_2$ and PPh$_3$. The UV spectra of [Co(SCN)$_2$(PPh$_3$)$_2$]-Zn-ZnBr$_2$ in these solutions showed the same absorption bands as those of Co(SCN)$_2$ in the solutions except for the absorption bands attributed to triphenylphosphine.

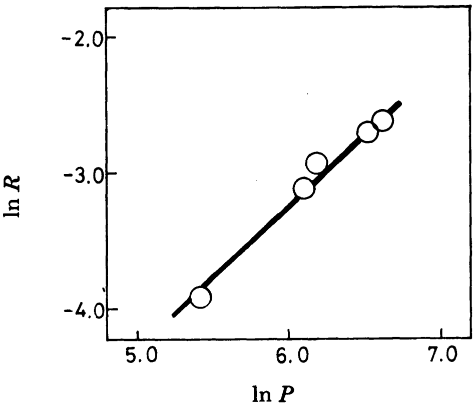


Fig. 3. Effect of hydrogen pressure; P: hydrogen pressure/mmHg, R: rate/ml(S.T.P.) min^{-1} (1 mmHg = 133.2 Pa).

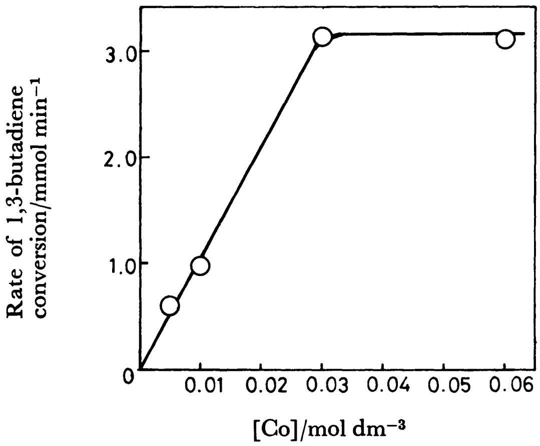


Fig. 4. Effect of the initial concentration of [Co(SCN)$_2$(PPh$_3$)$_2$].

Ethers can be typed into two groups, one is cyclic ethers and the other is acyclic polyethers. Acyclic ethers gave higher cis-selectivity than cyclic ones. The increase of n in CH$_3$O(CH$_2$CH$_2$O)$_n$CH$_3$ leads to the increase of cis-selectivity and the decrease of hydrogenation rate (Fig. 5). In a mixture of THF and glyme (ratio 1:1), THF controlled the hydrogenation rate and selectivity. The coordination strength of cyclic ethers toward the cobalt complex is larger than that of acyclic ethers. When crown ether (18-crown-6) was added to glyme (crown:Co=1:1 and 10:1) the hydrogenation rates were a little slower than that in glyme alone without change of selectivity. The high cis-selectivity in acyclic ethers seems to be attributed to the weak chelate coordination of free movable oxyetylene units.

Deuteration. Deuteration of 1,3-butadiene gave 3,4-dideuterio-1-butene **1** and *cis*-1,4-dideuterio-2-butene **2** which were identified by their ^{13}C NMR spectra. Hydrogen was selectively introduced into 1,3-butadiene *via* 1,2- and 1,4-addition. The isotopic effect is calculated as r_H/r_D=1.4. Hydrogenation products of 1,3-butadiene in H$_2$–D$_2$ mixed gas (ratio of H$_2$/

Table 2. Solvent effects on the hydrogenation of 1,3-butadiene[a)]

Solvent	Rate/ml min^{-1}	Butene composition/%	
		1-Butene	*cis*-2-Butene
Glyme	0.10	18	82
Diglyme	0.06	17	83
THF	0.08	53	47
Tetrahydropyran	0.04	45	55
1,3-Dioxolane	0.15	45	55
Dioxane	0.01	40	60
Glyme+THF (1 : 1)	0.11	51	49
Glyme+18-crown-6			
(Co : crown = 1 : 1)	0.03	20	80
(Co : crown = 1 : 10)	0.04	17	83

a) Solvent 10 ml, [Co] 0.03 mol dm^{-3}, 1,3-butadiene 2.0 mmol at 17 °C.

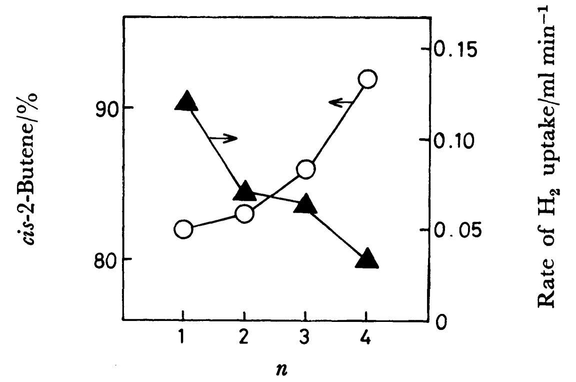
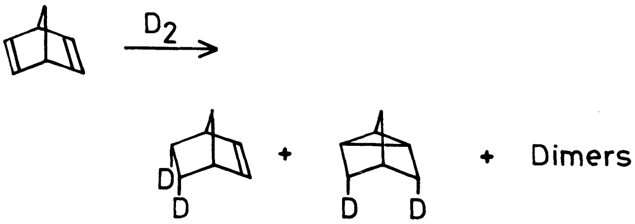


Fig. 5. Solvent effects on the hydrogenation of 1,3-butadiene ; solvents CH$_3$O(CH$_2$CH$_2$O)$_n$ CH$_3$.

D_2=1.08) were **1**, **2**, 1-butene and *cis*-2-butene. Mono- and polydeuterated products were not observed, so molecular identity was maintained.

Deuteration of norbornadiene was tried to investigate the stereochemistry of the addition of hydrogen. *endo, endo*-5,6-Dideuteriotricyclo[2.2.1]hept-2-one **3** and *endo,endo*-3,5-dideuteriotricyclo[2.2.1.$0^{2,5}$]heptane **4**, which were identified by their ^{1}H NMR spectra by comparison of those of authentic samples,[13] were obtained to ensure that hydrogen was added selectively via cis-endo-addition.



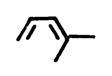
3 4

Methyl-substituted Effect on Acyclic Conjugated Dienes. We compared the rates of hydrogenation of methyl-substituted 1,3-butadienes (Table 3). The hydrogenation of C_1- or/and C_4-substituted 1,3-butadienes was faster than that of 1,3-butadiene, while the hydrogenation of C_1 or/and C_4-substitued 1,3-butadienes was slower. The substitution of methyl group at C_2 as seen in isoprene accelerates the hydrogenation rate 2.3 times as fast as that of 1,3-butadiene. 2,3-Dimethyl-1,3-butadiene can be estimated to be hydrogenated faster than 1,3-butadiene by a factor of 2.3^2=5.3 which is in fair agreement with the experimental value.

On the other hand, C_1- or C_4-subtituted methyl group lowers the hydrogenation rate by 1/23 time. The hydrogenation rate of *trans,trans*-2,4-hexadiene can be estimated to be $1/23^2$=0.002 time of that of 1,3-butadiene. The value is regarded as nearly zero. No hydrogenation of *trans,trans*-2,4-hexadiene occurred in practice. The hydrogenation rate of *trans*-2-methyl-1,3-pentadiene can be estimated to be 2.3× 1/23=0.1 time of that of 1,3-butadiene. The value almost agrees with the experimental one on the basis of the order.

α-Angle Effect on the Hydrogenation of Cyclic Conjugated Dienes. The reason why cyclopentadiene, 1,3-cyclohexadiene and 1,3-cycloheptadiene were hydrogenated but 1,3-cyclooctadiene not, may be related to α-angles of cyclic dienes (Table 4). The hydrogenation rate is almost independent of β-angles. Strohmeier

TABLE 3. HYDROGENATION OF CONJUGATED ACYCLIC DIENES

Diene	Substituent				Relative rate
	C_1	C_2	C_3	C_4	
	H	Me	Me	H	5.0
	H	Me	H	H	2.3
	H	H	H	H	1.0
	H	Me	H	Me	0.2
	H	H	H	Me	0.04
	H	H	H	Me,Me	0.03
	Me	H	H	Me	0

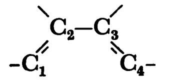
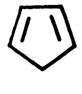
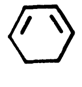
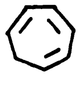
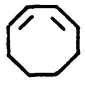
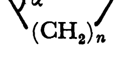


TABLE 4. HYDROGENATION OF CONJUGATED CYCLIC COMPOUNDS

Compound	Relative rate		α-Angle[a]	β-Angle[a]
	[Co(SCN)(PPh$_3$)$_3$]	*[Co(CN)$_5$]$^{3-}$* [a]		
	1.0	1.0	109	110
	0.47	1.67	120.6	116.5
	0.003	0.71	121.8	127
	0	0	(126.46)[b]	(126.46)[b]

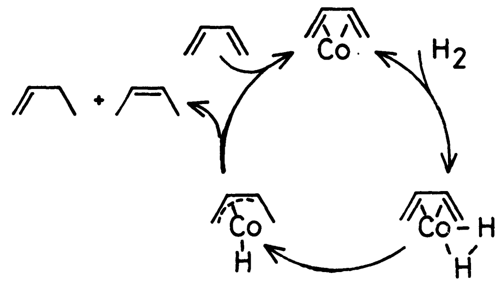


a) By Strohmeier and Iglauer.[15] b) Angle of cyclooctatetraene.

and Iglauer explained the ease of the hydrogenation of cyclic dienes by $[Co(CN)_5]^{3-}$ in terms of the strain energy of carbon-carbon bonding.[15]

Although no hydrogenation of 1,3- and 1,5- cyclooctadiene occurred, 1,5-cyclooctadiene was isomerized even in the absence of hydrogen. Hydrogen is not required for the isomerization of cyclooctadiene. The isomerization may occur *via* a 1,3-hydrogen shift with a π-allylcobalt hydride intermediate. The hydrogenation rates decrease in the order cyclopentadiene>1,3-cyclohexadiene>1,3-cycloheptadiene≫1,3-cyclooctadiene. The smaller α-angle is, the more reactive the cyclic diene is. The ease of hydrogenation of cyclic dienes with small α-angle is related to the facile approach of hydrogen coordinated with cobalt toward coordinated dienes. Because α-angles are related to the distances between the C_1 and C_4 carbons of conjugated dienes and cobalt. On the crystallographic studies the distances between cobalt and C_1-carbon of π-cyclopentadienyl-1-phenylcyclopentadiene cobalt was 1.97 Å,[16] while that of *cis*-di-μ-carbonyl-bis[carbonyl-(π-cyclohexa-1,3-diene)cobalt] was 2.13 Å.[17]

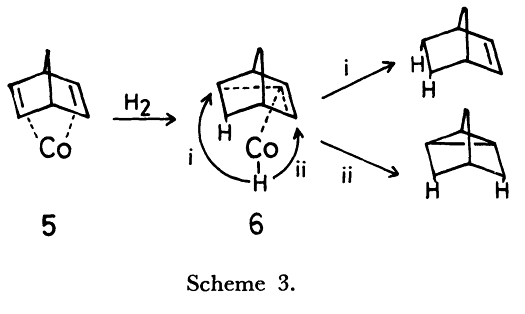
Mechanism of Hydrogenation. A monomeric cobalt complex is an active species due to the first dependence of the cobalt concentration. The catalytic species must be [Co(SCN)(PPh$_3$)$_3$]. Zero-order dependence of butadiene indicates that the reaction between Co(I) complex and butadiene gives cobalt(I)–butadiene π-complex (Scheme 2). Hydrogen adds to the complex to form *anti*-1-methyl-π-allylcobalt hydride complex. Since *trans*-2-butene was not formed at all, no scrambling of the anti-complex to the syn-isomer occurred.[18] *anti*-π-Allylcobalt hydride complex produces *cis*-2-butene and 1-butene to regenerate the initial cobalt(I) complex.



Co ≡ [Co(SCN)(PPh$_3$)$_n$]

Scheme 2.

In the case of norbornadiene, cobalt(I)-norbornadiene complex **5** is formed (Scheme 3). Then hydrogen reacts with the complex to form the delocalized nortricyclenylcobalt hydride complex **6**. When the hydride reacts *via* path I, norbornene is produced, and *via* path II, nortricyclene is produced.



Scheme 3.

We are grateful to Dr. Sadayuki Mori of Chemical Research Institute, Kyoto University for performing mass spectrometric measurements.

References

1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 4th ed., John Wiley and Sons, New York (1980), pp. 779—783.

2) *e.g.*, Stereoelectronic effects of molecules-five coordinated complexes of transition metals. S. Otsuka, *Kagaku* (*Chemistry, Kyoto*) **34**, 202 (1979).

3) a) G. N. Schrauzer, J. H. Weber, and T. M. Beckham, *J. Am. Chem. Soc.*, **92**, 7078 (1979); b) L. Vaska, L. S. Chen, and W. V. Miller, *ibid*, **93**, 6671 (1971); c) K. Kawakami, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **51**, 21 (1978); d) K. Kawakami, T. Mizoroki, and A. Ozaki, *J. Mol. Catal.*, **5**, 175 (1979); e) G. Fachinetti, C. Floriani, P. F. Zanazzi, and A. R. Zanzari, *Inorg. Chem.*, **18**, 3469 (1979); f) H. Kanai and K. Ishii, *Bull. Chem. Soc. Jpn.*, **54**, 1015 (1981); g) H. Kanai, *J. Mol. Catal.*, **12**, 231 (1983); h) H. Kanai, N. Yamamoto, K. Kishi, K. Mizuno, and K. Tarama, *J. Catal.*, **73**, 228 (1982).

4) R. B. Moffett, *Org. Synth.*, Coll. Vol. IV, 238 (1963).

5) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

6) A. Rosenheim and R. Cohn, *Z. Anorg. Chem.*, **27**, 289 (1901).

7) R. D. Rieke, S. J. Uhm, and P. M. Hudnall, *J. Chem. Soc., Chem. Commun.*, **1973**, 269.

8) R. D. Rieke, P. T. Li, T. P. Burns, and S. T. Uhm, *J. Org. Chem.*, **46**, 4323 (1981).

9) F. Toda and K. Iida, *Chem. Lett.*, **1976**, 695.

10) E. N. Frankel and R. O. Butterfield, *J. Org. Chem.*, **34**, 3930 (1969).

11) R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 706 (1970).

12) a) M. J. Mirbach, T. Nyu Pyu, and A. Saus, *J. Organomet. Chem.*, **236**, 309 (1982); b) G. Platbrood and L. Wilputte-Steinert, *J. Organomet. Chem.*, **70**, 393 (1974); c) M. J. Mirbach, D. Steinmetz, and A. Saus, *J. Organomet. Chem.*, **168**, C13 (1979).

13) H. Kanai, Y. Watabe, and T. Nakayama, 49th National Meeting of the Chemical Society of Japan, Tokyo, Apr. 1984, Abstr., No. 3P05.

14) a) N. H. Werstiuk, *Can. J. Chem.*, **48**, 2310 (1970); b) G. Platbrood and L. Wilputte-Steinert, *Bull. Soc. Chim. Belg.*, **82**, 733 (1973).

15) W. Strohmeier and N. Iglauer, *Z. Phys. Chem.*, **61**, 29 (1968).

16) M. R. Churchill and R. Mason, *Proc. R. Soc. London*,

Ser. A, **279**, 191 (1964).
17) F. S. Stephens, *J. Chem. Soc., Dalton,* **1972**, 1752.
18) W. Rupilius and M. Orchin, *J. Org. Chem.,* **36**, 3604 (1971).