A Study of the Interactions between Free Radicals and Cobalt Complexes

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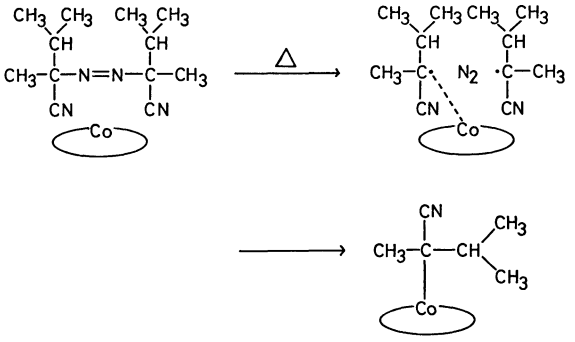
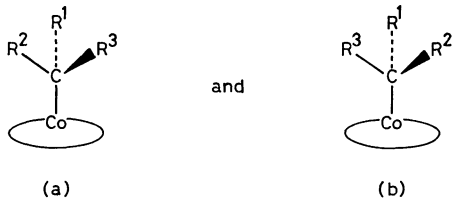
The interaction between free radicals and cobalt complexes (Co(II)TPP and Co(II)(sal)$_2$(*R*-CHXDA)) has been studied using (*S,S*)-(−)-, (*R,R*)-(+)-, and *meso*-1,1′-diphenylazoethane as a radical source. The decomposition of *meso*-1,1′-diphenylazoethane by heat or UV-light in the presence of Co(II)(sal)$_2$(*R*-CHXDA) having an asymmetric ligand produced an optically active (+)-2,3-diphenylbutane. The suggestion is that the α-methylbenzyl radical formed from the azo compound is stereoselectively stabilized by the Co(II)(sal)$_2$(*R*-CHXDA).

The literature cites several addition reactions of polyhaloalkanes to olefins using organometallic catalysts, 1:1 adducts being formed in good yield. In the absence of the organometallic complex, there is negligible formation of the 1:1 adducts.[1] Nagai *et al.*[2] postulated that the reaction proceeded *via* a free radical mechanism and concluded that the high selectivity in the 1:1 adduct was a direct consequence of the restricted freedom of movement of a radical which was restrained in the coordination sphere of the complex. Furthermore, Murai *et al.*[3] reported an optically active adduct in the addition reactions of bromotrichloromethane to 1-alkenes using a rhodium complex with (−)-diop as the asymmetric ligand.

It accepted that a free radical is stabilized by reacting with several metal ions (including metal complexes).[4] For example, the radicals derived from the decomposition reactions of several azo compounds are stabilized in the presence of metal complexes, especially cobalt, such as Co(II)TPP and Co(II)(sal)$_2$(*R*-CHXDA).[5]



Therefore, it may be possible for a metal complex having an asymmetric ligand to stabilize radicals in two stereochemically different formes as follows:



(a) (b)

Either of these two stabilized radicals, (**a**) or (**b**), will enter a reaction preferentially owing to the difference in their reactivities resulting in the formation of an optically active product. The interactions between radicals and metal complexes, especially the effect of interaction on the yield and specific rotation of 2,3-diphenylbutane, have been studied using (*S,S*)-(−)-, (*R,R*)-(+)-, and *meso*-1,1′-diphenylazoethane as the radical source and Co(II)(sal)$_2$(*R*-CHXDA) as the asymmetric metal complex.

Experimental

Materials. The azo compounds ((*S,S*)-(−)-, (*R,R*)-(+)-, and *meso*-1,1′-diphenylazoethane[6]) and the metal complexes (Co(II)TPP and Co(II)(sal)$_2$(*R*-CHXDA)[6]) have been prepared as described in a previous paper. (−)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((−)-diop) has been prepared according to the method of Kagan *et al.*[7] The (−)-diop-Rh(I) has been prepared by mixing (−)-diop and di-μ-chloro-bis(π-1,5-cyclooctadiene)dirhodium(I) in benzene under nitrogen.

Decomposition of Azo Compound. The decomposition of the azo compounds in the presence or absence of metal complex has been conducted as described in a previous paper.[6] In the photo-decomposition reactions, the azo compound, contained in an ampoule under nitrogen was decomposed completely by UV-light and the volume of nitrogen released was measured.

Analysis of Decomposition Products. 2,3-Diphenylbutane, a coupling product, was separated by TLC (hexane-silica gel) and the optical rotation was measured. 2,3-Diphenylbutane was qualitatively analyzed by PMR and GC-MS.[6]

Quantitative analyses of the decomposition products were conducted by GLC (Silicone DC-550). The column temperatures were 120 °C for the non-coupling products (styrene and ethylbenzene) and 200 °C for the coupling product (2,3-diphenylbutane).

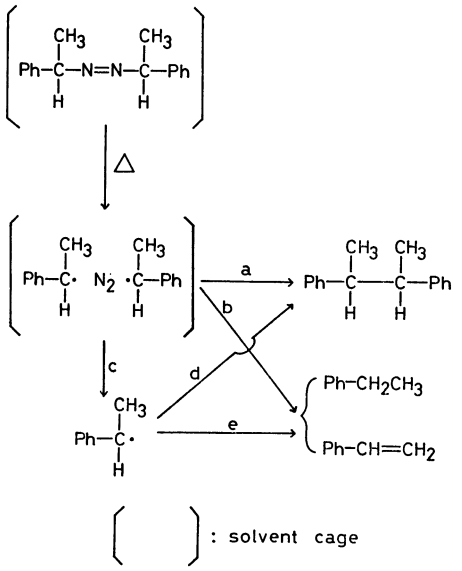
Measurement of Decomposition Rates. The decomposition rates of the azo compounds were measured as described in a previous paper.[6]

Measurement of Visible Spectra. The visible spectra of benzene solutions containing the cobalt complex (Co(II)-TPP or Co(II)(sal)$_2$(*R*-CHXDA)), (*S,S*)-(−)-1,1′-diphenylazoethane and/or nitrosobenzene were measured under nitrogen using 1 mm thick quartz glass cell.

Results and Discussion

Decomposition of 1,1′-Diphenylazoethane. According to a previous report,[6] the decomposition products from the thermolysis of 1,1′-diphenylazoethane (Azo compound) in the absence of metal complex were 2,3-diphenylbutane, styrene, and ethylbenzene. In the presence of a metal complex, an additional product, namely acetophenone α-methylbenzylhydrazone was formed.

The formation mechanism[8] of these products may be illustrated by Schemes 1 and 2.



Scheme 1.

Routes **a** and **b** show the coupling and disproportionation reactions of the two radicals in a classical solvent cage, respectively. Routes **d** and **e** are, on the other hand, the corresponding reactions for radicals diffused from the cage. Scheme 2 is a possible route for the decomposition reaction in the presence of the metal complex as reported previously.[6]

The amount of 2,3-diphenylbutane formed was less in the presence of the complex, since a part of the starting azo compound was converted into acetophenone α-methylbenzylhydrazone (Scheme 2). The complex can interact with three types of radical such as $PhC\dot{H}(CH_3)$, $Ph-\dot{C}(CH_3)-N=N-CH(CH_3)Ph$, and $Ph-C(\dot{C}H_3)=N-\underset{\cup}{\dot{N}}-CH(CH_3)Ph$. In the presence of nitrosobenzene, the only radical produced was the α-methylbenzyl radical; no acetophenone α-methylbenzylhydrazone was produced (Table 1). In order to understand the interaction between the complex and

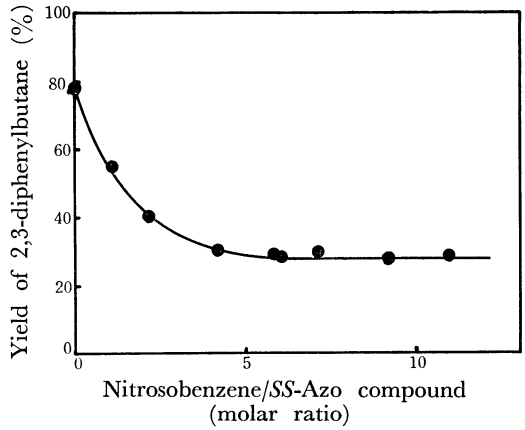
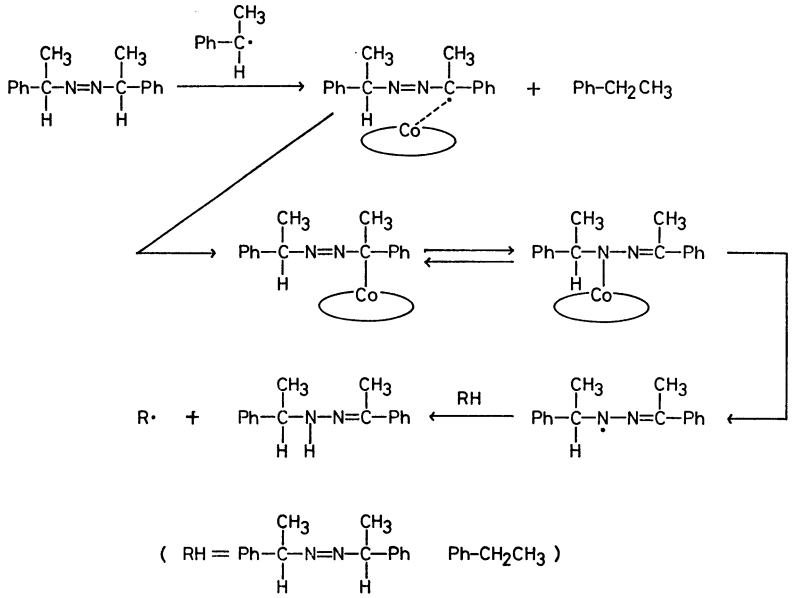


Fig. 1. Yield of 2,3-diphenylbutane in the presence of nitrosobenzene. Reaction conditions: in benzene at 104 °C for 2 days; *SS*-Azo compound: 3.7×10^{-2} M.

the α-methylbenzyl radical, the thermal decomposition has been examined in the absence and presence of nitrosobenzene.

2,3-Diphenylbutane Obtained in the Presence of Nitrosobenzene. (*S,S*)-1,1′-Diphenylazoethane (*SS*-Azo compound) was thermally decomposed in the presence of nitrosobenzene with and without the metal complex. Figure 1 illustrates the effect of nitrosobenzene on the yield of 2,3-diphenylbutane and as may be seen, the yield of 2,3-diphenylbutane decreases with the increase in the concentration of nitrosobenzene, up to six times the amount of azo compound. After this, the yield of 2,3-diphenylbutane did not vary, even in the presence of a great excess of nitrosobenzene. Twenty eight percent of 2,3-diphenylbutane is estimated to be formed in the solvent cage. Under these conditions, a trace amount of the disproportionation products was obtained and no acetophenone α-methylbenzylhydrazone was formed, even in the presence of the metal complex (Table 1).

From the result in Fig. 2, it appears there



Scheme 2.

Table 1. Specific rotation and yield of 2,3-diphenylbutane formed in the presence of nitrosobenzene

Run	Azo compd ($\times 10^2$ M)		Metal complex ($\times 10^4$ M)		Nitroso-benzene ($\times 10$ M)	Products (%)					
						$PhCH_2CH_3$	$PhCH{=}CH_2$	Ph-CH(Me)-CH(Me)-Ph	Ph-CH(Me)-N-N-CH(Me)-Ph		$[\alpha]_D^{b)}$ of coupling product
1	*SS*	4.2		0	3.27	trace	trace	28.0	0		−28.4
2	*RR*	4.2		0	3.27	trace	trace	28.4	0		+28.5
3	*SS*	4.5	CoTPP	3.4	3.10	trace	trace	26.5	0		−28.5
4	*SS*	4.2	Co*	7.6	3.27	trace	trace	24.4	0		−29.0
5	*RR*	4.2	Co*	7.6	3.27	trace	trace	27.7	0		+29.3
6	*meso*[a)]	7.5	Co*	53.0	4.75	trace	trace	21.7	0		−0.9

Reaction conditions: 104 °C (a): 80 °C) in benzene for 2 days (a): 7 days).
b) Measured in benzene at 20 °C. Co*: Co(II)(sal)$_2$(*R*-CHXDA).

Table 2. Decomposition rate of azo compounds in the presence of cobalt complex in benzene at 70 °C

Azo compd	Complex	Complex/Azo compd (molar ratio)	Obsd (mol s^{-1})
SS	0	0	1.11×10^{-6}
SS	Co*	2.7×10^{-3}	1.5×10^{-6}
SS	Co(II)TPP	8.2×10^{-3}	1.4×10^{-6}

Co*: Co(II)(sal)$_2$(*R*-CHXDA).
SS-Azo compound: 2.15×10^{-1} M.

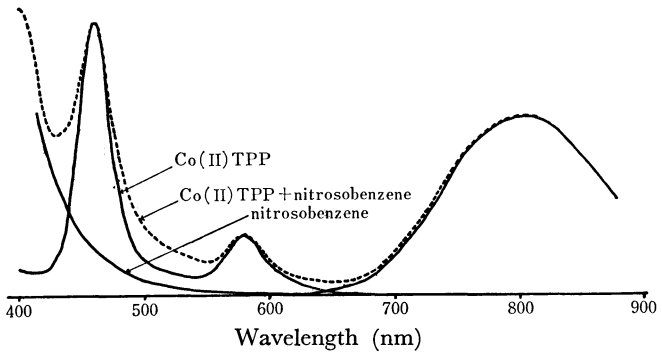


Fig. 2. Visible spectra of Co(II)TPP and/or nitrosobenzene in benzene at 20 °C. Co(II)TPP: 8.45×10^{-5} M, nitrosobenzene: 3.74×10^{-2} M.

is little, if any, interaction between nitrosobenzene and the cobalt complex, the spectrum of the binary system being a simple overlapping of the two individual spectra.

There is however, evidence which suggests a possible interaction between the metal complex and the Azo compound: (1) the visible spectra of a benzene solution of the *SS*-Azo compound and the cobalt complexes exhibited isosbestic points (Figs. 3(a) and (b)), a part of the Azo compound, at least, being thought to react with the cobalt complex, and (2) the decomposition rate of the Azo compound in the presence of a metal complex is higher than that in the absence of the metal complex (Table 2). The increase in the rate is regarded as a consequence of the increased reactivity of the Azo compound which interacts with the cobalt complex.

The specific rotation and yield of 2,3-diphenylbutane obtained from the *RR* and *SS*-Azo compounds in the

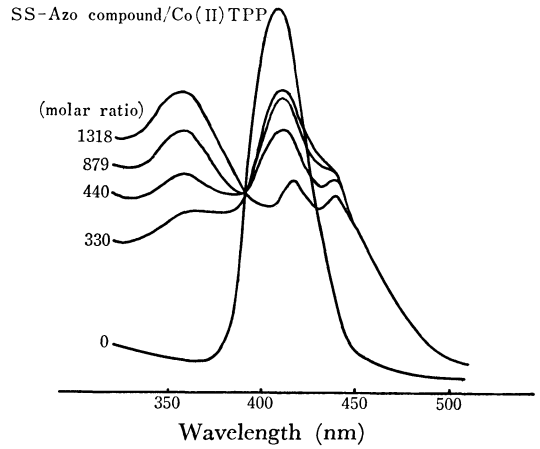


Fig. 3(a). Visible spectra of Co(II)TPP in the presence of *SS*-Azo compound in benzene at 20 °C. Co(II)TPP: 8.45×10^{-5} M.

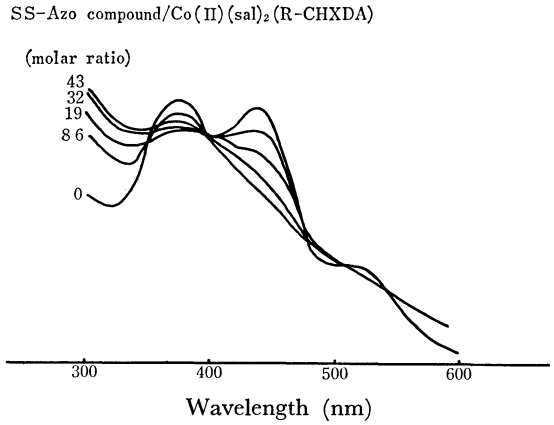
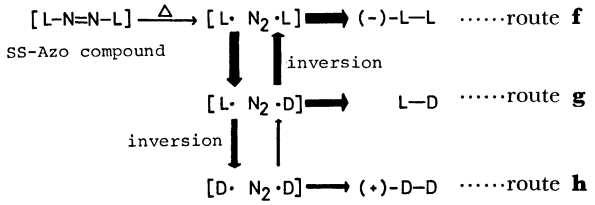


Fig. 3(b). Visible spectra of Co(II)(sal)$_2$(*R*-CHXDA) in the presence of *SS*-Azo compound in benzene at 20 °C. Co(II)(sal)$_2$(*R*-CHXDA): 5.65×10^{-4} M.

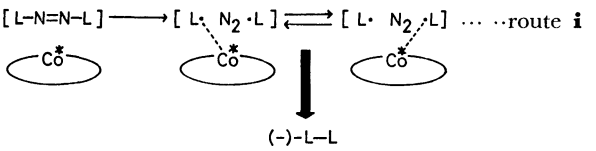
presence of both Co(II)(sal)$_2$(*R*-CHXDA) and nitrosobenzene are shown in Figs. 4 and 5, respectively. In the coupling reaction within a solvent cage, the value of $[\alpha]_D$ and the yield of 2,3-diphenylbutane, derived from the *RR*-Azo compound were negligibly changed. Little dependency upon the concentration of Co(II)-(sal)$_2$(*R*-CHXDA) was established. In the case of

the *SS*-Azo compound, however, an increase in the concentration of the metal complex caused a decrease in both the yield and the optical rotation (Fig. 4). The results may be explained by assuming the following mechanism: In the absence of the metal complex, the *SS*-Azo compound is decomposed as shown in Scheme 3, and the product consists of three coupled compounds, L-L, D-D, and L-D. Therefore, the specific rotation of the product will depend on the relative rates of coupling and inversion.[8]

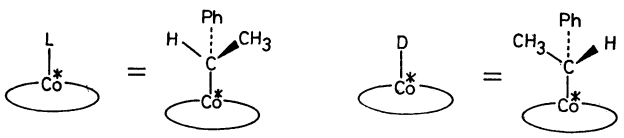


Scheme 3.

In the presence of Co(II)(sal)$_2$(*R*-CHXDA), the radicals within a solvent cage may interact with the metal complex as discussed above and consequently, the inversion and coupling reactions will be more difficult for these radicals. The results shown in Figs. 4 and 5 suggest, therefore, that the ratio of (−)-2,3-diphenylbutane ((−)-L-L) obtained from reaction route **i** is greater than that from reaction route **f** as in Scheme 3.



The cobalt complex, Co(II)(sal)$_2$(*R*-CHXDA), may have greater interaction with a radical from the *SS*-Azo compound compared with that from the *RR*-Azo compound, a more favorable stabilization operating in Form **A** than Form **B**.



Form A Form B

The decrease in optical rotation of 2,3-diphenylbutane from the *SS*-Azo compound (Fig. 4) may be explained by assuming that the radical formed from the *SS*-Azo compound is immediately stabilized by the Co(II)-(sal)$_2$(*R*-CHXDA) and that the inversion is suppressed. Since the stabilized radical on the complex less readily undergoes coupling, the yield of coupled product decreases.

2,3-Diphenylbutane Obtained in the Absence of Nitrosobenzene. The mechanism of formation of 2,3-diphenylbutane outside the solvent cage may be elucidated using the *meso*-Azo compound in place of the *RR* and *SS*-Azo compounds. Table 3 shows the yield and the $[\alpha]_D$ of 2,3-diphenylbutane formed from the

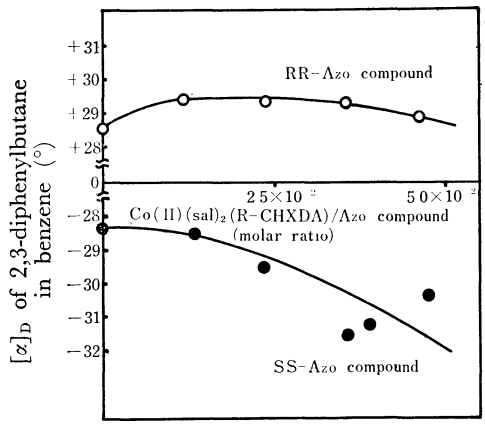


Fig. 4. The specific rotation of 2,3-diphenylbutane formed from Azo compound in the presence of Co(II)-(sal)$_2$(*R*-CHXDA) and nitrosobenzene.
Reaction conditions: Azo compound: 4.2×10^{-2} M nitrosobenzene: 3.27×10^{-1} M in benzene at 104 °C for 4 days.

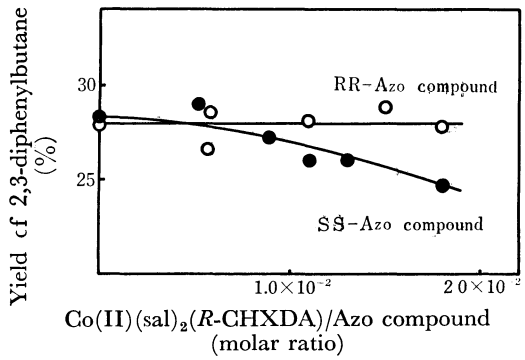


Fig. 5. Yield of 2,3-diphenylbutane formed from Azo compound in the presence of Co(II)(sal)$_2$(*R*-CHXDA) and nitrosobenzene.
Reaction conditions: Azo compound: 4.2×10^{-2} M; nitrosobenzene: 3.27×10^{-1} M, in benzene at 104 °C for 4 days.

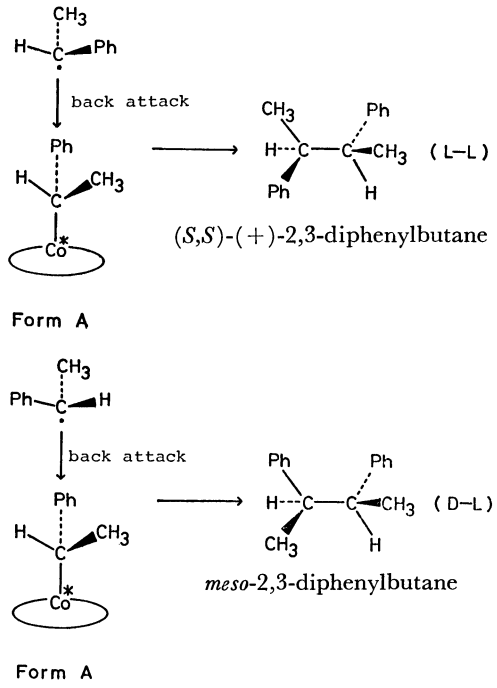
meso-Azo compound in the presence of an optically active complex such as Co(II)(sal)$_2$(*R*-CHXDA) or (−)-diop-Rh(I). 2,3-Diphenylbutane formed in the presence of Co(II)(sal)$_2$(*R*-CHXDA) or (−)-diop-Rh(I) was optically active. With the former metal complex, the optical rotation of 2,3-diphenylbutane obtained in the absence of nitrosobenzene showed an opposite and higher absolute value compared to that obtained in the presence of nitrosobenzene (Table 1, run 6). This suggests that the major part of the optical rotation of 2,3-diphenylbutane formed in the absence of nitrosobenzene is ascribable to 2,3-diphenylbutane which was formed by the stereoselective coupling reaction of diffused radicals outside the solvent cage. The diffused radicals stereoselectively stabilized by the metal complex (probably Form **A**) are considered to undergo coupling with the other radicals with inversion of stereochemistry as shown in Scheme 4.

In the presence of nitrosobenzene, because there are relatively few diffusion radicals, the reaction in the cage predominates to form (−)-2,3-diphenylbutane as shown in route **i**.

Table 3. Specific rotation and yield of 2,3-diphenylbutane formed in the absence of nitrosobenzene

Run	*meso*-Azo compd ($\times 10^2$ M)	Metal complex ($\times 10^4$ M)	Decompn method	2,3-diphenylbutane			
				Yield (%)	$[\alpha]_D^{a)}$		e. e. (%)[8]
1	4.8	0	Δ	95.0	0	(c=0.53)	0
2	7.8	Co* 6.1	Δ	97.0	+0.8	(c=1.47)	0.8
3	4.6	Co* 3.6	Δ	98.0	+1.6	(c=1.27)	1.6
4	4.3	Co* 6.1	Δ	79.9	+2.1	(c=1.22)	2.1
5	5.4	Co* 6.1	Δ	68.3	+1.4	(c=1.50)	1.4
6	3.9	Co* 6.1	Δ	50.8	+1.6	(c=0.44)	1.6
7	5.3	Co* 3.4	*hν*	93.4	+0.2	(c=1.31)	0.2
8	5.1	Co* 6.8	*hν*	85.9	+0.3	(c=0.70)	0.3
9	4.0	Co* 6.8	*hν*	85.3	+0.3	(c=1.03)	0.3
10	8.5	Co* 16.0	*hν*	84.0	+0.9	(c=1.10)	0.9
11	4.8	(−)-diop-Rh(I) 1.2	*hν*	97.6	−0.9	(c=0.74)	0.9
12	4.2	(−)-diop-Rh(I) 2.5	*hν*	96.4	−0.5	(c=1.52)	0.5

Reaction conditions: {Δ: 82 °C in benzene for 4 days. *hν*: 30 °C in benzene by irradiating UV-light for 30 min.
Co*: Co(II)(sal)$_2$(*R*-CHXDA). a): Measured in benzene at 20 °C.



Scheme 4.

Conclusion. This study has revealed that an organometallic complex having asymmetric ligands stabilizes a free radical from an Azo compound and produces stereoselective coupling products. The optical yield of the coupling product is very low, but the optical purity may be improved by controlling the rate of decomposition of the azo compound, thereby increasing the possibility of interaction between the free radical and the complex. The use of metal complexes having more suitable chirality is another method of attaining a high value of optical purity of product.

References

1) M. Asscher and D. Vofsi, *J. Chem. Soc.*, **1963**, 1887, 3921; **1964**, 4962.
2) H. Matsumoto, T. Nakano, K. Takasu, and Y. Nagai, *J. Org. Chem.*, **43**, 1734 (1978).
3) N. Sonoda, S. Murai, R. Sugise, and K. Kondo, 26th IUPAC Congress Abstracts Session I, 93 (1978).
4) J. K. Kochi, "Free Radicals," Wiley-Interscience (1973), Vol. I, pp. 626, 627.
5) K. Yoshino, Y. Ohkatsu, and T. Tsuruta, *Polym. J.*, **9**, 275 (1977).
6) K. Yoshino, Y. Ohkatsu, and T. Tsuruta, *Bull. Chem. Soc. Jpn.*, **52**, 1738 (1979).
7) H. B. Kagan and T. -P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972).
8) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 867 (1970).