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Redox Reactions of *cis*-Dialkylcobalt(III) Complexes with Benzyl and Allyl Bromides, Induced by Thermal Cleavage of the Cobalt-Carbon Bond

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The thermal cleavage of the cobalt-carbon bond of *cis*-dialkylcobalt(III) complexes, *cis*-$[R_2Co(bpy)_2]^+$(R=Me, Et, and $PhCH_2$; bpy=2,2′-bipyridine), was enhanced by the presence of benzyl and allyl bromide, inducing the C-C bond formation to yield mainly 1,2-diphenylethane and 1,5-hexadiene, respectively. In the *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$-allyl bromide system, a comparable amount of the cross-coupling product (4-phenyl-1-butene) was obtained together with the homo-coupling products (1,2-diphenylethane and 1,5-hexadiene). The enhancement of the thermal cleavage of the cobalt-carbon bond of *cis*-$[R_2Co(bpy)_2]^+$ by the reactions with benzyl and allyl bromides is caused by the high reactivity of the carbanion ligand of $[RCo(bpy)_2]^+$ produced by the homolytic cleavage of the cobalt-carbon bond of *cis*-$[R_2Co(bpy)_2]^+$, which undergoes the exchange, coupling, and cross-coupling reactions with benzyl and allyl groups of the bromides. Based on the kinetics and the activation parameters, the cobalt-carbon bond dissociation enthalpy of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ has been estimated to be 92 kJ mol^{-1}.

The mechanisms of thermal decomposition of organotransition-metals[1,2] as well as the bond dissociation energies of the metal-carbon bonds[3] have been subjects of much interest, since the application of transition-metal reagents to organic, organometallic, and biochemical synthesis, stoichiometric or catalytic, requires the cleavage of metal-carbon bonds. Significant attention has been devoted to mono-organocobalt complexes, which relate to the naturally occurring coenzyme, vitamin B_{12}.[4-8] Although cobalt-carbon bonds of many mono- and di-organocobalt(III) complexes are thermally stable at moderate temperatures, the cleavage of cobalt-carbon bonds is known to be enhanced significantly by redox reactions with organic and inorganic oxidants.[9-13] The cleavage of cobalt-carbon bonds of di-organocobalt(III) complexes, which has been much less studied than mono-organocobalt(III) complexes, is of particular interest, since the cleavage of the cobalt-carbon bond may produce coordinately unsaturated mono-organocobalt(II) complexes which may be much more reactive than di-organocobalt complexes.[14,15]

We have previously reported that the photocleavage of cobalt-carbon bonds of *cis*-dialkylcobalt(III) complexes, *cis*-$[R_2Co(bpy)_2]^+$ (R=Me, Et, and $PhCH_2$; bpy=2,2′-bipyridine), induces C-C bond formation via the redox reactions with benzyl and allyl bromides to yield 1,2-diphenylethane and 1,5-hexadiene, respectively, as the main products.[16] In this study, we report that the thermal cleavage of the cobalt-carbon bond of *cis*-$[R_2Co(bpy)_2]^+$ also induces the C-C bond formation in redox reactions with benzyl and allyl bromides. The present study provides a nice opportunity to compare the thermal and photochemical redox reactions of *cis*-dialkylcobalt(III) complexes with organic halides, revealing both the common and the different aspects in mechanisms between the thermal and photochemical redox reactions.

Experimental

Materials. *cis*-Dialkylcobalt(III) complexes, *cis*-$[R_2Co(bpy)_2]^+$ (R=Me, Et, and $PhCH_2$), were prepared by the reaction of $CoCl_2 \cdot 6H_2O$ with an excess of $NaBH_4$ in the presence of the corresponding alkyl halides and the ligand bpy.[16,17] They were isolated as the perchlorate salts and recrystallized from methanol/water. The purity of the complexes was checked by the elemental analysis; *cis*-$[Me_2Co(bpy)_2]ClO_4$: Found: C, 52.7; H, 4.6; N, 11.1. Calcd for $C_{22}H_{22}N_4O_4CoCl$: C, 52.8; H, 4.4; N, 11.2. *cis*-$[Et_2Co(bpy)_2]ClO_4$ H_2O: Found: C, 52.1; H, 5.1; N, 10.0. Calcd for $C_{24}H_{28}N_4O_5CoCl$: C, 52.7; H, 5.2; N, 10.2. *cis*-$[(PhCH_2)_2Co(bpy)_2]ClO_4$: Found: C, 62.0; H, 4.6; N, 8.5. Calcd for $C_{34}H_{30}N_4O_4CoCl$: C, 63.0; H, 4.7; N, 8.7. Both $[Co(bpy)_3](ClO_4)_2$ and $[Co(bpy)_3]ClO_4$ were prepared by following the literature method.[18] Benzyl or allyl bromide obtained from Wako Pure Chemicals was washed with a 5% aqueous $NaHCO_3$ solution and water successively. After the solution was dried with $MgSO_4$, it was fractionally distilled in the dark under reduced pressure before use. Reagent grade acetonitrile was purified by the standard procedure,[19] followed by redistillation from calcium hydride. Acetonitrile-d_3 was stirred with freshly activated Molecular Sieve 4A (Wako Pure Chemicals) and then transferred in vacuum. Other reagents used for the product analyses were obtained commercially.

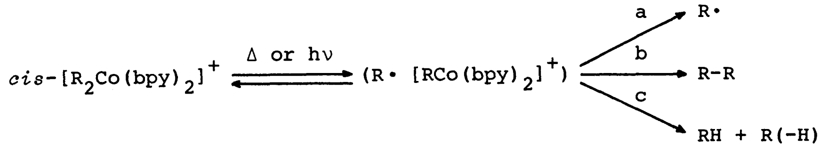
Analytical Procedure. Thermal decomposition of *cis*-$[R_2Co(bpy)_2]^+$ was carried out in a Pyrex tube (8 mm I.D.) which contained an MeCN solution (0.5 cm^3) of *cis*-$[R_2Co(bpy)_2]^+$ (1.0×10^{-2} mol dm^{-3}). The solution in the tube was thoroughly degassed by the repeated freeze-pump-thaw cycles before sealing. The top of sealed tube was covered with a reflux condenser and the bottom containing the solution was immersed in an oil bath which was thermostated at 353 K. After the reaction for 52 h, an atmospheric pressure of nitrogen was introduced to the tube, and the gaseous products were analysed by glc using a Unibeads 1S column (1 m).

The redox reactions of *cis*-$[R_2Co(bpy)_2]^+$ with benzyl and allyl bromides were monitored using a Japan Electron Optics JNM-PS-100 ^{1}H NMR spectrometer (100 MHz). Typically, *cis*-$[R_2Co(bpy)_2]^+$ (0.05 mmol) and benzyl bromide

Table 1. Product Distributions of Thermal and Photochemical Decomposition of *cis*-$[R_2Co(bpy)_2]^+$ under Degassed Conditions in Acetonitrile

cis-$[R_2Co(bpy)_2]^+$	Reaction	Time	Conversion	Product distribution
		h	%	%
R=Me[a]	Δ[c]	52	22	CH_4(66), C_2H_6(34)
	$h\nu$[d]	15	91	CH_4(91), C_2H_6(9)
R=Et[a]	Δ[c]	52	79	C_2H_6(67), C_2H_4(24), C_4H_{10}(9)
	$h\nu$[d]	15	76	C_2H_6(73), C_2H_4(27), C_4H_{10}(trace)
R=PhCH$_2$[b]	Δ[c]	5	57	$PhCH_3$(94), PhC_2H_4Ph(6),
	$h\nu$[d]	50	43	$PhCH_3$(47), PhC_2H_4Ph(51)

a) 1.0×10^{-2} mol dm^{-3}. b) 4.5×10^{-2} mol dm^{-3}. c) Thermolysis at 353 K. d) Photolysis was carried out under irradiation with visible light from a Xenon lamp through a Toshiba glass filter (O-36) which transmits light of λ>360 nm at 298 K (Ref. 16).



Scheme 1.

(0.05 mmol) was added to an NMR tube which contained 0.5 cm^3 CD_3CN. After the solution was degassed, the sealed NMR tube with a reflux condenser was immersed in an oil bath at 353 K. The NMR spectra were measured periodically at 298 K and the products were identified by comparing the spectra with those of authentic samples. The conversion of *cis*-$[R_2Co(bpy)_2]^+$ to $[Co(bpy)_3]^{2+}$ was confirmed by the appearance of the down field signals of the 2,2′-bipyridine ligand.[18] The organic products were analysed by glc using an OV-17 column (2 m).

Kinetic Measurements. Kinetic data were obtained by using a Union SM-401 spectrophotometer equipped with thermostated cell holders. Reaction rates were determined by the disappearance of the absorption band due to *cis*-$[R_2Co(bpy)_2]^+$ in MeCN (λ_{max}=472, 495, and 502 nm for R=Me, Et, and PhCH$_2$, respectively) under a degassed condition using a Schlenk tube equipped with a side arm fused to a square cuvette (1 or 10 mm I.D.). All the data followed pseudo-first-order kinetics, from which rate constants were determined by least-squares curve fitting using an NEC 9801F microcomputer.

Results and Discussion

Thermal Decomposition of *cis*-$[R_2Co(bpy)_2]^+$. *cis*-Dialkylcobalt(III) complexes are stable in MeCN at 298 K. When the temperature was raised to 353 K, *cis*-$[R_2Co(bpy)_2]^+$ decomposed slowly to undergo the dealkylation reaction. The product distributions are shown in Table 1, together with the data of the corresponding photodecomposition[16] for comparison. The product distributions between thermal and photodecomposition of *cis*-$[R_2Co(bpy)_2]^+$ are similar to each other, except for the ratio of the coupling products of the alkyl groups. For example, both the thermolysis and photolysis of *cis*-$[Me_2Co(bpy)_2]^+$ give methane and ethane, but the mol ratio of ethane to methane in the thermolysis at 353 K (34/66) is significantly larger than that in the photolysis at 298 K (9/91). In the case of *cis*-$[Et_2Co(bpy)_2]^+$ as well, an appreciable amount of the coupling product (butane) is obtained only in the thermolysis (Table 1). On the other hands, thermolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ gives a smaller amount of the coupling product (1,2-diphenylethane) than the photolysis (Table 1).

Such product distributions between the thermolysis and photolysis may be explained by Scheme 1, where both the thermolysis and photolysis of *cis*-$[R_2Co(bpy)_2]^+$ results in the homolytic cleavage of the cobalt-carbon bond to produce a geminate radical pair (R• $[RCo(bpy)_2]^+$) which undergoes (a) free radical reactions out of the cage to yield RH and R-R, (b) a coupling reaction in the cage to yield R-R, or (c) a β-hydrogen transfer in the cage to give RH and R(-H) with a 1 : 1 ratio when the alkyl group contains a β hydrogen. Such a homolytic cleavage of the Co-C bond in the photolysis of *cis*-$[R_2Co(bpy)_2]^+$ has been confirmed by the detection of alkyl radicals in the ESR measurements at 77 K.[16] In the case of R=Me or Et, the alkyl radical formed in the geminate radical pair may be reactive enough to undergo the coupling reaction in the cage at a high temperature (e.g., 353 K) to yield more coupling product R-R than the case of photolysis at 298 K. On the other hand, the activation barrier of hydrogen abstraction by benzyl radical from a solvent is known to be higher than that of bimolecular coupling reaction of benzyl radicals.[20] Thus, in the case of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, the former becomes a major process in the thermolysis at 353 K to yield mainly toluene (Table 1). Although the stepwise homolytic processes (Scheme 1) appear to account for the product distribution in both the thermal and photochemical decomposition of *cis*-$[R_2Co(bpy)_2]^+$ in the absence and presence of benzyl or allyl bromide as discussed later in more detail, the present conclusion that the coupling R-R and olefin R(-H) products arise

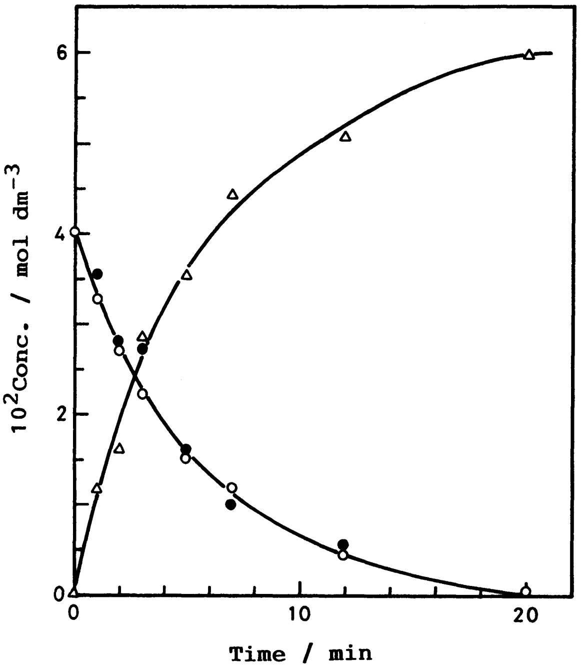


Fig. 1. Time course of the thermal reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (4.0×10^{-2} mol dm^{-3}) with benzyl bromide (4.0×10^{-2} mol dm^{-3}) under a degassed condition in CD_3CN at 353 K; *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), and PhC_2H_4Ph (△).

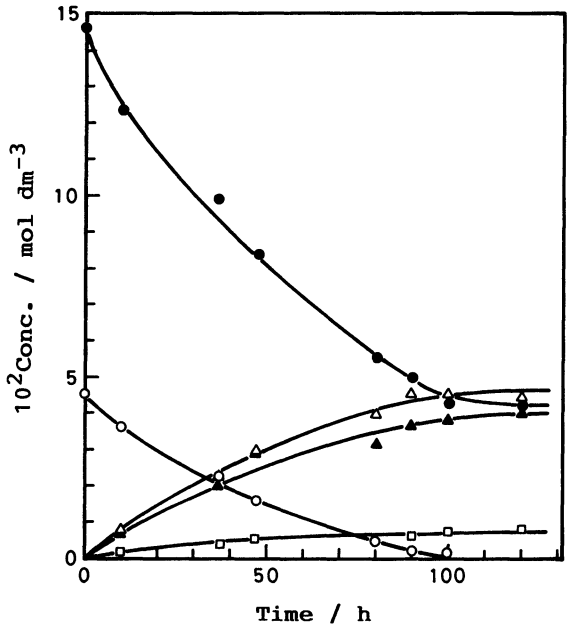


Fig. 2. Time course of the thermal reaction of *cis*-$[Me_2Co(bpy)_2]^+$ (4.5×10^{-2} mol dm^{-3}) with benzyl bromide (1.46×10^{-1} mol dm^{-3}) under a degassed condition in CD_3CN at 353 K; *cis*-$[Me_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), MeBr (△), PhC_2H_4Ph (▲), and C_2H_6 (□).

via the homolytic cleavage of the cobalt-carbon bond must be accepted with reservation, since the concerted processes for the reductive coupling and *β*-elimination pathways are difficult to distinguish from the stepwise, homolytic processes.[21-24)]

Redox Reactions of *cis*-$[R_2Co(bpy)_2]^+$ with Benzyl and Allyl Bromides. When the thermal decomposition of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ is carried out in the presence of benzyl bromide at 353 K, the rate is enhanced significantly as shown in Fig. 1, where the reaction is completed in 20 min. In addition, the product distribution is changed drastically from toluene as a main product in the absence of benzyl bromide to 1,2-diphenylethane in the presence of benzyl bromide (Fig. 1). The approximate stoichiometry of the reaction is given by Eq. 1,

$$cis\text{-}[(PhCH_2)_2Co(bpy)_2]^+ + PhCH_2Br \xrightarrow{\Delta} \frac{3}{2}PhC_2H_4Ph + [Co(bpy)_2Br]^+ \quad (1)$$

which is the same as the corresponding photochemical reaction.[16)]

Thermolysis rate of *cis*-$[Me_2Co(bpy)_2]^+$ is also enhanced by the presence of benzyl bromide, although the rate is much slower than that of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, as shown in Fig. 2. The presence of benzyl bromide suppresses completely the formation of methane observed in the absence of benzyl bromide (Table 1), instead methyl bromide is formed as well as 1,2-diphenylethane as a main product, while the ethane formation is not suppressed completely (Fig. 2). The apparent stoichiometry of the reaction between *cis*-$[Me_2Co(bpy)_2]^+$ and benzyl bromide is 1 : 2.3. Such a stoichiometry in Fig. 2 may be explained by considering the occurrence of two different reactions; one is the same as the corresponding photochemical reaction (Eq. 2),[16)]

$$cis\text{-}[Me_2Co(bpy)_2]^+ + 3PhCH_2Br \longrightarrow \frac{3}{2}PhC_2H_4Ph + 2MeBr + [Co(bpy)_2Br]^+, \quad (2)$$

where *cis*-$[Me_2Co(bpy)_2]^+$ reacts with three equivalent amounts of benzyl bromide to yield 1,2-diphenylethane and methyl bromide, and the other is the reaction with a 1 : 1 stoichiometry to yield ethane (Eq. 3),

$$cis\text{-}[Me_2Co(bpy)_2]^+ + PhCH_2Br \longrightarrow \frac{1}{2}PhC_2H_4Ph + [Co(bpy)_2Br]^+ + C_2H_6, \quad (3)$$

where benzyl bromide may be reduced by $[Co(bpy)_2]^+$ following the coupling reaction in the cage (Scheme 1-b). The occurrence of two different reactions (Eqs. 2 and 3) can also account for the product distribution in the thermolysis of *cis*-$[Et_2Co(bpy)_2]^+$ in the presence of benzyl bromide (Fig. 3), where one mol of *cis*-$[Et_2Co(bpy)_2]^+$ reacts with 1.4 mol of benzyl bromide to yield 1,2-diphenylethane, ethyl bromide, and butane with small amounts of toluene and ethylene.

Similar results are obtained in the thermolysis of *cis*-$[R_2Co(bpy)_2]^+$ in the presence of allyl bromide. Table 2 summarizes the product distribution includ-

Table 2. Product Yields in the Thermal Reactions of *cis*-$[R_2Co(bpy)_2]^+$ with Benzyl and Allyl Bromides under Degassed Conditions in Acetonitrile at 353 K

cis-$[R_2Co(bpy)_2]^{+a)}$	R'Br^a)^	Time h	Product %^b)^
R=Me (4.5×10^{-2})	R'=$PhCH_2$ (1.46×10^{-1})	103	PhC_2H_4Ph(49), $PhCH_3$(1.0), C_2H_6(33), MeBr(98)
R=Et (9.6×10^{-2})	R'=$PhCH_2$ (9.6×10^{-2})	54	PhC_2H_4Ph(48), $PhCH_3$(2.1), C_4H_{10}(38), C_2H_4(10), EtBr(23)
R=Me (7.1×10^{-2})	R'=C_3H_5 (7.1×10^{-2})	100	C_6H_{10}(48), C_3H_6(3.3), C_4H_8(2.2), C_2H_6(32), MeBr(98)
R=Et (9.5×10^{-2})	R'=C_3H_5 (9.5×10^{-2})	30	C_6H_{10}(49), C_3H_6(1.8), C_5H_{10}(2.2), C_4H_{10}(37), C_2H_4(10), EtBr(22)
R=$PhCH_2$ (4.0×10^{-2})	R'=$PhCH_2$ (4.0×10^{-2})	0.5	PhC_2H_4Ph(147), $PhCH_3$(5.4)
R=$PhCH_2$ (4.0×10^{-2})	R'=C_3H_5 (4.0×10^{-2})	0.5	PhC_2H_4Ph(86), C_6H_{10}(35), PhC_4H_7(17), $PhCH_3$(12), C_3H_6(4.3)

a) The concentrations of the reactants in parentheses. b) Based on the cobalt complex.

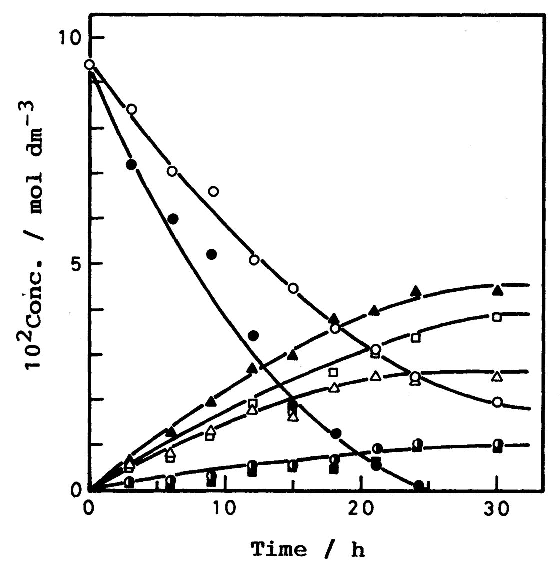
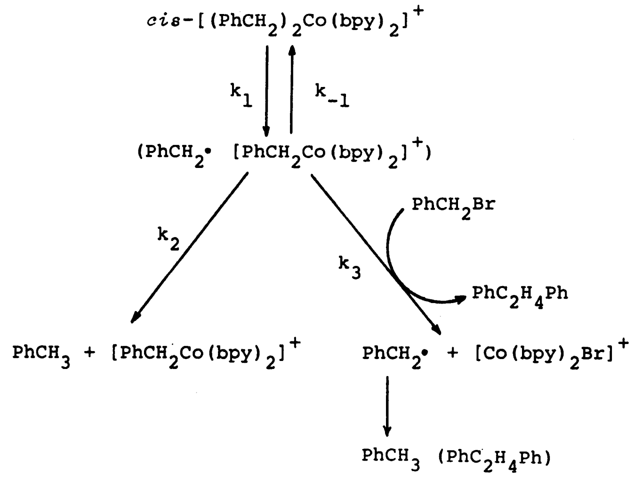


Fig. 3. Time course of the thermal reaction of *cis*-$[Et_2Co(bpy)_2]^+$ (9.4×10^{-2} mol dm^{-3}) with benzyl bromide (9.4×10^{-2} mol dm^{-3}) under a degassed condition in CD_3CN at 353 K; *cis*-$[Et_2Co(bpy)_2]^+$ (○), $PhCH_2Br$ (●), EtBr (△), PhC_2H_4Ph (▲), C_4H_{10} (□), C_2H_4 (■), and $PhCH_3$ (◑).

ing the minor products. In the reactions of *cis*-$[Me_2Co(bpy)_2]^+$ and *cis*-$[Et_2Co(bpy)_2]^+$ with benzyl and allyl bromides, the coupling products of the organic groups of the bromides (1,2-diphenylethane and 1,5-hexadiene, respectively) are obtained, and small amounts of cross-coupling products between the alkyl group of *cis*-$[R_2Co(bpy)_2]^+$ and the organic group of the bromides (e.g., ethylbenzene in the *cis*-$[Me_2Co(bpy)_2]^+$-benzyl bromide system) are formed as well as the products derived from hydrogen abstraction by benzyl and allyl radicals from a solvent (i.e., toluene and propene, respectively). The stoichiometry of these reactions is between 1 and 3 on the degree of the contribution of two different reactions (Eqs. 2 and 3). In the case of the reactions of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide, however, the stoichiometry is 1 : 1 (Eq. 1) to yield mainly the homo-coupling product (1,2-diphenylethane) together with a small amount of toluene. When benzyl bromide is replaced by allyl bromide in the reaction with *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, the cross-coupling product between benzyl and allyl group, i.e., 4-phenyl-1-butene is formed together with the homo-coupling products (1,2-diphenylethane and 1,5-hexadiene) as shown in Table 2. Thus, the thermolysis of all the *cis*-dialkylcobalt(III) complexes in the presence of benzyl or allyl bromide results in the C–C bond formation to yield the homo- or cross-coupling products of benzyl and allyl groups as the main products together with small amounts of products derived from hydrogen abstraction by benzyl or allyl radical from a solvent.

Kinetics and Mechanism. The rate of thermal decomposition of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ at 353 K is the fastest among *cis*-$[R_2Co(bpy)_2]^+$, and decreases in the order R=$PhCH_2$>Et>Me. The detailed kinetic study has been limited to the thermolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, since only *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ decomposed at measurable rates at relatively low temperatures (e.g., 323 K). The decomposition rates in both the absence and presence of benzyl bromide obeyed the pseudo-first-order kinetics, and the observed rate constant was increased significantly by the presence of benzyl bromide. Such enhancement of the rate by the presence of benzyl bromide may be explained by Scheme 2, where the cleavage of the cobalt-carbon bond (k_1 in Scheme 2) occurs to give a geminate radical pair ($PhCH_2\cdot[PhCH_2Co(bpy)_2]^+$). In the absence of benzyl bromide, the overall decomposition rate may be much lowered owing to the facile recombination of benzyl radical with $[PhCH_2Co(bpy)_2]^+$ in the cage (k_{-1}).[24] The recombination between free benzyl radical and $[PhCH_2Co(bpy)_2]^+$, which are escaped from the cage, may be neglected compared with the recombination of the geminate radical pair in Scheme 2, since the former unimolecular process may be much faster than the latter bimolecular process. Applying the steady-state approximation



Scheme 2.

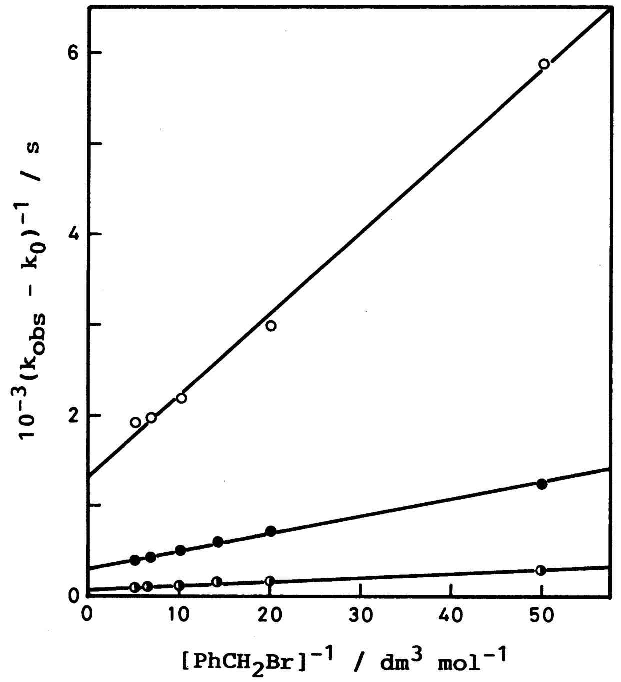


Fig. 4. Plots of $(k_{obsd}-k_0)^{-1}$ vs. $[PhCH_2Br]^{-1}$ for the thermal reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ (1.1×10^{-2} mol dm^{-3}) with benzyl bromide in MeCN at 323 (○), 338 (●), and 353 K (◑); see Eq. 7 in text.

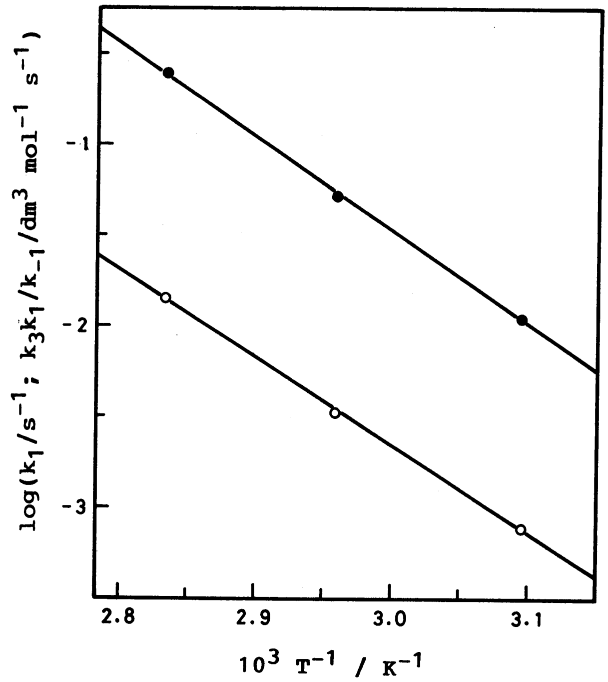


Fig. 5. Arrhenius plots of k_1 (○) and k_3k_1/k_{-1} (●) for the thermal reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide in MeCN.

to the intermediate $(PhCH_2\cdot[PhCH_2Co(bpy)_2]^+)$ in Scheme 2, the observed rate constant k_0 in the absence of benzyl bromide is expressed by Eq. 4,

$$k_0 = k_1k_2/(k_{-1}+k_2), \tag{4}$$

where k_2 is the rate constant for hydrogen abstraction by benzyl radical from a solvent to yield toluene. Since the recombination process (k_{-1}) may be highly exothermic, k_{-1} may be much larger than k_2; $k_{-1}\gg k_2$, when Eq. 4 is reduced to Eq. 5.

$$k_0 = k_1k_2/k_{-1} \tag{5}$$

The benzyl group of $[PhCH_2Co(bpy)_2]^+$ produced by the homolytic cleavage of the cobalt-carbon bond of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ is regarded as the benzyl anion ligand on the basis of the ESR spectrum of $[PhCH_2Co(bpy)_2]^+$ observed in the photolysis of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ at 77 K.[15,16] Thus, in the presence of benzyl bromide, the benzyl anion ligand of $[PhCH_2Co(bpy)_2]^+$ may undergo the facile coupling reaction with benzyl bromide (k_3) to yield 1,2-diphenylethane as the case of the photoredox reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with benzyl bromide.[16] Then, the observed rate constant k_{obsd} in the presence of benzyl bromide may be given by Eq. 6. Under the

$$k_{obsd} = \frac{k_1(k_2 + k_3[PhCH_2Br])}{k_{-1} + k_2 + k_3[PhCH_2Br]} \tag{6}$$

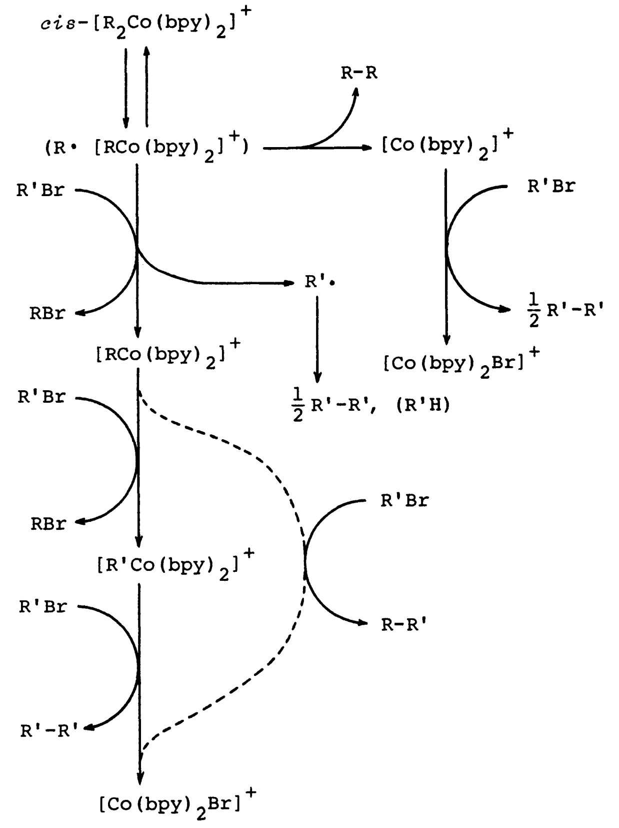
condition that $k_{-1}\gg k_2$, from Eqs. 5 and 6 is derived Eq. 7.

$$\frac{1}{k_{obsd} - k_0} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_3[PhCH_2Br]} \tag{7}$$

The validity of Eq. 7 is confirmed by the linear plots between $(k_{obsd}-k_0)^{-1}$ and $[PhCH_2Br]^{-1}$ at various temperatures as shown in Fig. 4. The rate constant k_1 and k_3k_1/k_{-1} at 323 are obtained as 7.7×10^{-4} s^{-1} and 1.1×10^{-2} dm^3 mol^{-1} s^{-1}, respectively. The rate constant k_{-1} for the cage recombination of an alkyl radical and cob(II)alamin has been reported to be 1.39×10^9 s^{-1}.[5b)] By using this value, the rate constant k_3 for the redox reaction of $[PhCH_2Co(bpy)_2]^+$ with benzyl bromide is estimated as 2.0×10^{10} dm^3 mol^{-1} s^{-1}, which is identical with the diffusion rate constant in MeCN.[25] Arrhenius plots of both k_1 and k_3k_1/k_{-1} give good straight lines with similar slopes to each other (Fig. 5), from which the values of $\Delta H^{\ddagger}_{1}$ and $\Delta H^{\ddagger}_{3}+\Delta H_{1}$ are obtained as 92 ± 4 and 96 ± 4 kJ mol^{-1}, respectively.

Thus, the cobalt-carbon bond dissociation enthalpy ΔH_1 is estimated as 92 ± 4 kJ mol^{-1} by assuming that $\Delta H^{\ddagger}_{-1}\cong 0$, which is a reasonable approximation for the highly exothermic radical recombination process.[5,6,24] The ΔH_1 value obtained here is similar to those of many organocobalt(III) complexes reported in the literatures.[3a,5,6] The $\Delta H^{\ddagger}_{3}$ value may also be estimated as 4 ± 4 kJ mol^{-1} from the values of ΔH_1 and $\Delta H^{\ddagger}_{3}+\Delta H_1$. Such a small $\Delta H^{\ddagger}_{3}$ value is compatible with the rate constant k_3 being diffusion controlled as described above. The facile reaction of $[PhCH_2Co(bpy)_2]^+$ with benzyl bromide may be responsible for the efficient C–C bond formation from *cis*-$[R_2Co(bpy)_2]^+$ and benzyl bromide, induced by the thermal cleavage of the cobalt-carbon bond. A cobalt-containing product $[Co(bpy)_2Br]^+$, which may be the initial product by the reaction of $[PhCH_2Co(bpy)_2]^+$ with benzyl bromide as confirmed by the ESR spectrum in the photolysis of the *cis*-$[R_2Co(bpy)_2]^+$-benzyl bromide system at 77 K,[16] is converted to $[Co(bpy)_3]^{2+}$ being the most stable form among the mono-, bis-, and tris(2,2′-bipyridine)cobalt(II) complexes (see Experimental).[26] On the other hand, benzyl radicals produced by the homolytic cleavage of the cobalt-carbon bond of *cis*-$[R_2Co(bpy)_2]^+$ give 1,2-diphenylethane and a small amount of toluene (Table 2).[27] According to Scheme 2, the stoichiometry of the thermal reaction of *cis*-$[R_2Co(bpy)_2]^+$ with benzyl bromide is 1 : 1, agreeing with the observation in Fig. 1 (Eq. 2).

When the alkyl groups of the reactants (*cis*-$[R_2Co(bpy)_2]^+$ and R′Br) are different, the reaction scheme becomes more complicated as shown in Scheme 3, where the thermolysis of *cis*-$[R_2Co(bpy)_2]^+$ (R=Me and Et) also leads to the homolytic cleavage of the cobalt-carbon bond to produce the geminate radical pair $(R\cdot[RCo(bpy)_2]^+)$. In the presence of R′Br (R′=$PhCH_2$ and C_3H_5), the alkyl radical (Me· and Et·) may be converted to the more stable radical ($PhCH_2\cdot$ and $C_3H_5\cdot$) by the reaction with R′Br as confirmed by the ESR spectrum in the photolysis of the *cis*-$[R_2Co(bpy)_2]^+$-R′Br system at 77 K.[16] The benzyl and allyl radicals give the homo-coupling products (1,2-diphenylethane and 1,5-hexadiene, respectively) with small amounts of by-products derived from the hydrogen abstraction from a solvent (toluene and propene, respectively) as shown in Table 2. The carbanion ligand in $[RCo(bpy)_2]^+$ may react readily with R′Br to produce the more stable carbanion ligand, and $[R'Co(bpy)_2]^+$ thus formed by the exchange reaction may undergo the homo-coupling reaction with R′Br to yield R′–R′ and $[Co(bpy)_2Br]^+$, while $[RCo(bpy)_2]^+$ may proceed also to the cross-coupling reaction with R′Br, which is shown by the broken line in Scheme 3, yielding R–R′ as a minor product in Table 2 (ethylbenzene, propylbenzene, 1-butene, and 1-pentene for the *cis*-$[Me_2Co(bpy)_2]^+$-$PhCH_2Br$, *cis*-$[Et_2Co(bpy)_2]^+$-$PhCH_2Br$, *cis*-$[Me_2Co(bpy)_2]^+$-C_3H_5Br, and *cis*-$[Et_2Co(bpy)_2]^+$-C_3H_5Br systems, respectively). In this case, the stoichiometry of the reaction of *cis*-$[R_2Co(bpy)_2]^+$ with R′Br is 1 : 3 (Eq. 2), in contrast with the case in Scheme 2.



Scheme 3.

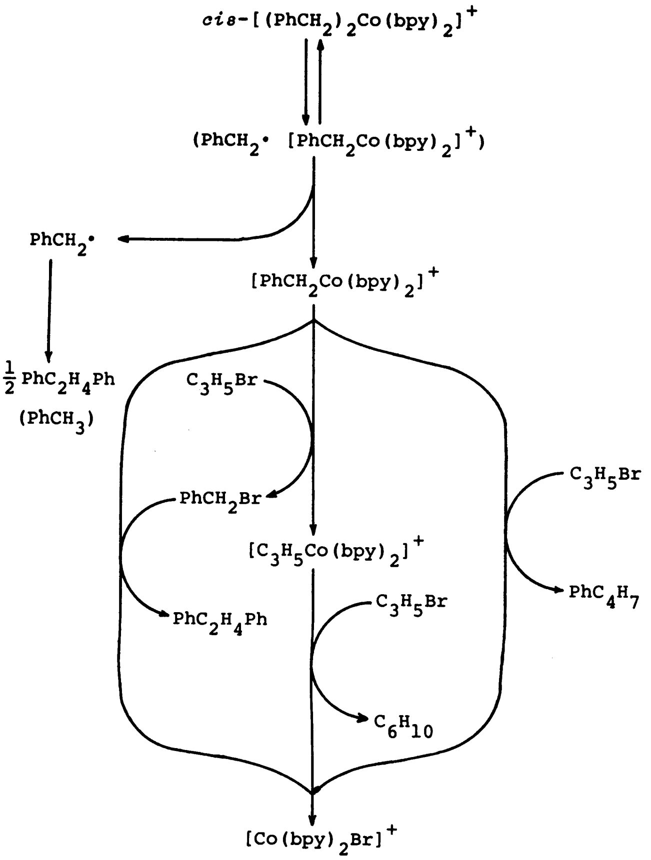
On the other hand, a coupling reaction in the geminate radical pair produced by the homolytic cleavage of the cobalt-carbon bond of *cis*-$[R_2Co(bpy)_2]^+$ may occur in the case of R=Me and Et to yield R–R and $[Co(bpy)_2]^+$ (Scheme 1-b).[28] A β-hydrogen transfer in the geminate radical pair may also occur in the case of R=Et which has a β-hydrogen to yield ethane and ethylene as well as $[Co(bpy)_2]^+$ (Scheme 1-c). In the presence of R′Br, such processes are suppressed by the facile reaction of $[RCo(bpy)_2]^+$ in the geminate radical pair with R′Br, but the reductive coupling process is not suppressed completely to yield R–R as well as $[Co(bpy)_2]^+$ which may readily reduce R′Br to give R′–R′ (Scheme 3). Although the reaction mechanism for the reduction of R′Br by $[Co(bpy)_2]^+$ is less clear than that for the reduction of R′Br by $[RCo(bpy)_2]^+$, a likely pathway may be proposed as shown by Eqs. 8—10, since the facile reduction of

$$[Co(bpy)_2]^+ + R'Br \longrightarrow [Co(bpy)_2Br]^+ + R'\cdot, \tag{8}$$

$$R'\cdot + [Co(bpy)_2Br]^+ \longrightarrow [R'Co(bpy)_2Br]^+, \tag{9}$$

$$R'\cdot + [R'Co(bpy)_2Br]^+ \longrightarrow R'\text{-}R' + [Co(bpy)_2Br]^+, \tag{10}$$

alkyl halides by Co(I) complexes is known to occur to yield alkyl radicals and Co(II) complexes Eq. 8,[29] and



Scheme 4.

the coupling reaction of alkyl radicals may be enhanced in the presence of $[Co(bpy)_2Br]^+$ by the fast recombination with alkyl radicals (Eq. 9),[5,6,24] followed by the bimolecular homolytic displacement reactions (Eq. 10).[23,30] In this case, the stoichiometry is 1 : 1 (Eq. 3). Thus, these two different processes (Eqs. 2 and 3) in Scheme 3 can account for the observed stoichiometry as well as the product distribution in the reaction with R′Br (Figs. 2, 3, and Table 2).

Although the thermal reaction of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ with allyl bromide (Scheme 4) is the most complicated case, the reaction scheme is identical with that for the corresponding photochemical reaction reported in the previous paper,[16] except that the thermal cleavage of the cobalt-carbon bond occurs instead of the photocleavage. The monobenzylcobalt(II) complex $[PhCH_2Co(bpy)_2]^+$ produced by the thermal cleavage of the cobalt-carbon bond of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$ can undergo the exchange, homo- coupling, and cross-coupling reactions with comparable rates, because of similar stabilities between benzyl and allyl anions, yielding 1,2-diphenylethane and 1,5-hexadiene as the homo-coupling products as well as 4-phenyl-1-butene as the cross-coupling product (Table 2). The benzyl radicals which are also produced by the thermal cleavage of the cobalt-carbon bond give 1,2-diphenylethane and toluene by the bimolecular coupling reaction and the hydrogen abstraction from a solvent, respectively (Table 2).[27,31]

In conclusion, the present study has demonstrated that monoalkylcobalt(II) complexes produced by the thermal cleavage of the cobalt-carbon bond of *cis*-dialkylcobalt(III) complexes are highly reactive in the reduction of benzyl and allyl bromides, undergoing the C–C bond formation to yield the homo- and cross-coupling products depending on the stability of the carbanion ligand. In addition to this process which is essentially the same as employed in the corresponding photoredox reaction, the reductive elimination process, where the pair of cobalt-carbon bonds of *cis*-$[R_2Co(bpy)_2]^+$ is cleaved thermally, is also involved in the reduction of benzyl and allyl bromides.

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28) A cobalt-containing product was identified as $[\mathrm{Co(bpy)_3}]^+$ by comparing the nmr spectrum in the course of the thermolysis of *cis*-$[\mathrm{Et_2Co(bpy)_2}]^+$ in $\mathrm{CD_3CN}$ at 353 K with that of the authentic sample prepared by the reduction of $[\mathrm{Co(bpy)_3}]^{2+}$ with $\mathrm{NaBH_4}$ (see Ref. 18). The bis complex $[\mathrm{Co(bpy)_2}]^+$ formed initially may be converted to the tris complex being the most stable form (Ref. 26).

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